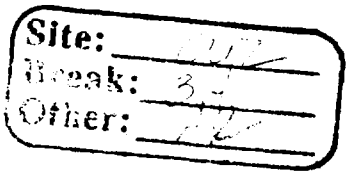
FINAL PLAN



19511

3 4 0144

ADDITIONAL ECOLOGICAL STUDIES OF OU-2 WORK PLAN

MCINTOSH PLANT SITE
OLIN CORPORATION
MCINTOSH, ALABAMA

Prepared for
Olin Corporation
McIntosh, Alabama

May 1994

WCC File 93N063C-1

Woodward-Clyde

Woodward-Clyde Consultants
2822 O'Neal Lane (70816)
P.O. Box 66317 (70896)
Baton Rouge, Louisiana

TABLE OF CONTENTS

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

1.0 INTRODUCTION

Olin Corporation is conducting a Remedial Investigation/Feasibility Study (RI/FS) at its McIntosh, Alabama facility under the oversight of the U. S. Environmental Protection Agency (EPA). The Olin McIntosh site is an active chemical production facility, [located approximately one mile east-southeast of the town of McIntosh, in Washington County, Alabama (Figure 1-1)], listed on the National Priority List (NPL) of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Olin signed an Administrative Order by Consent (AOC), effective May 9, 1990, with the EPA to perform the RI/FS. The RI report was submitted on July 30, 1993 (WCC, 1993). The baseline risk assessment (Section 6.0) was revised and resubmitted on December 21, 1993 and February 10, 1994. The RI report presented an assessment of the nature and extent of contamination and the human health and environmental risks from this contamination.

The AOC divided the site into two operable units (Figure 1-2). Operable Unit 1 (OU-1) is the plant area (all Olin property except OU-2). Operable Unit 2 (OU-2) is an approximate 65-acre basin on the floodplain of the Tombigbee River, the wetlands on Olin property around the basin, and the wastewater ditch leading to the basin. The RI/FS has been completed for OU-1. EPA has indicated that additional work is required in OU-2 to assess the risks that the site places on the surrounding environment. Olin submitted a draft Work Plan to EPA on September 3, 1993, describing the rationale and methodology for additional ecological studies in OU-2. EPA provided Olin with comments on the draft Work Plan on April 15, 1994. EPA's comments have been incorporated into this revised Work Plan in a manner agreed to during discussions between EPA and Olin.

1.1 BACKGROUND

As part of the baseline risk assessment (BRA) in the RI report, Olin submitted an ecological assessment (environmental evaluation) for OU-2. The ecological assessment was performed in conformance with current EPA guidance [*Risk Assessment Guidance*

for Superfund, Volume II, Environmental Evaluation Manual (U.S. EPA, 1989)]. Olin believes that the ecological assessment showed that overall, the vegetation and aquatic and terrestrial animal populations in OU-2 can be characterized as healthy. The extensive vegetative stress survey did not identify any impacts to individual plants or communities that could be attributed to site constituents. Results of benthic sampling suggested that the basin may not support as diverse a macroinvertebrate community as might generally be expected in similar systems, but no definite correlation was found between benthic composition and the distribution of site constituents. The concentrations of site constituents in the sediment and surface water might suggest possible effects to individual fish. However, no evidence was noted of such effects during the sampling performed for the RI. There were no obvious indications (either direct or indirect) that amphibian, reptile, bird, or mammal populations of OU-2 differ significantly (if at all) from those of similar areas off-site. The RI included a quantitative evaluation of the dietary exposures of four bird species and three mammal species known or expected to occur in OU-2. The evaluation consisted of relating known or estimated exposures to levels known or anticipated to be harmful, sometimes referred to as reference toxicity values (RTVs). With the exception of the estimated exposure of raccoons to DDTr, all of the potential dietary exposure (PDE) values were calculated in the RI report as one or more orders of magnitude below levels described as adequately protective of sensitive wildlife species. Newell and others (1987) suggested that a safe dietary concentration of DDTr for sensitive mammals would be 0.5 mg/kg, and the highest estimated exposure concentration for OU-2 (raccoon) was 0.15 mg/kg. In view of the dietary exposure calculations, Olin concluded it is improbable that terrestrial or amphibious higher vertebrate populations in OU-2 are adversely affected by exposures to site constituents via the ingestion pathway. Since the ingestion pathway is generally considered the most important for exposures of higher vertebrates to bioaccumulative chemicals, Olin also concluded the risks associated with other pathways (e.g., dermal contact with water or soil) in OU-2 are inconsequential.

On June 15, 1993, EPA notified Olin that tasks in addition to those outlined in the amended Work Plan would be necessary for OU-2 at the Olin Chemicals McIntosh Plant Site. EPA stated that the RI "lacked adequate detail to assess the risks that the Site placed on the surrounding environment," and additional sampling would be necessary in OU-2. EPA further stated that a work plan for OU-2 must be developed

by Olin and approved by EPA. Olin responded in a July 6, 1993 letter, indicating a willingness to perform necessary additional sampling in OU-2, and to cooperate with the agency to gather any additional necessary data. It is Olin's understanding that the purpose of the sampling is to collect data necessary to adequately characterize OU-2 for the purpose of developing and evaluating effective remedial alternatives, and that EPA needs these data before deciding on appropriate remedies for OU-2.

In a letter dated July 7, 1993, EPA provided Olin a scope for additional sampling of prey items (forage fish, crayfish, earthworm, and plant tubers) and an avian nesting study. At a meeting on July 7 to discuss this scope, EPA indicated that the avian nesting study was to be set aside for future consideration. This revised Work Plan includes the sampling requested by EPA.

1.2 PURPOSE AND SCOPE

This plan is designed to provide additional site-specific ecological exposure information upon which to base remedial decisions regarding OU-2. As noted above, the occurrence and distribution of certain ecological chemicals of potential concern (COPCs) within OU-2 were characterized during earlier phases of the Remedial Investigation (RI). The COPCs were determined to be mercury (Hg), hexachlorobenzene (HCB), and the pesticide DDT and its metabolites (DDD, DDE; collectively referred to as DDTr). Direct releases of the COPCs stopped several years ago, and the materials are largely sequestered in the aquatic sediments and floodplain soils of OU-2. On the basis of community-level measurements and estimates of exposures to selected receptors, Olin concluded that relatively minor, if any, adverse ecological effects have occurred or are likely to result from the presence of Hg, HCB, and DDTr in OU-2.

EPA has indicated that it will rely on tissue sample data for risk management decisions. The approach of this plan is to obtain additional exposure information for EPA's needs by collecting soil, water and tissue samples for COPC analysis. In addition to the COPC data, this revised Work Plan describes a food web model that will be used to predict exposures to receptors whose tissue is not analyzed for COPCs.

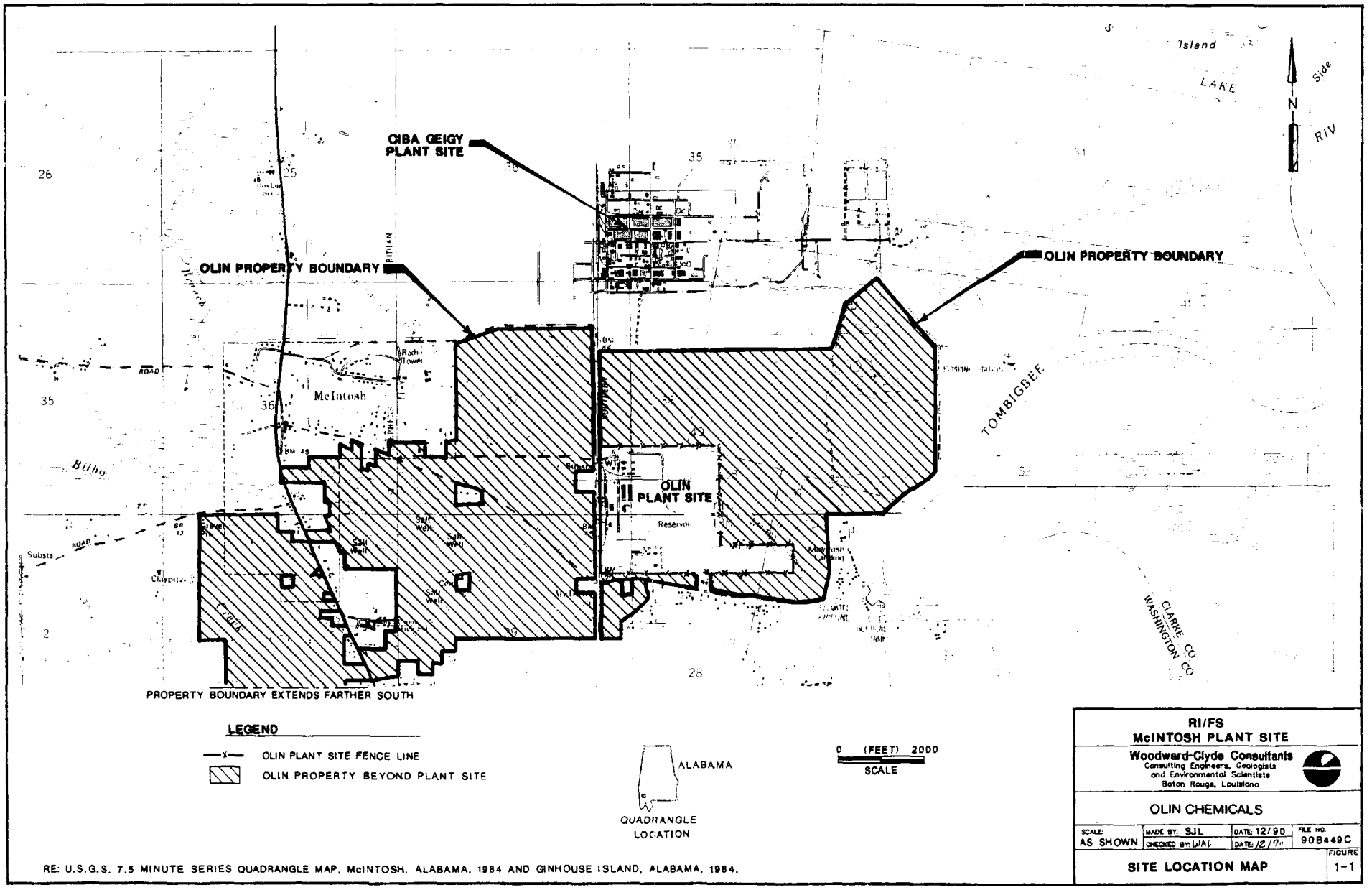
EPA has specified the following list of species to be included in the food web model:

Crayfish (*Orconectes* spp., invertebrate detritivore, prey item)
Mosquitofish (*Gambusia affinis*, piscine insectivore, forage fish/prey item)
Largemouth bass (*Micropterus salmoides*, upper trophic level aquatic receptor)
Raccoon (*Procyon lotor*, mammalian omnivore)
River Otter (*Lutra canadensis*, mammalian piscivore)
Prothonotary Warbler (*Protonotaria citrea*, avian insectivore)
Red-Winged Blackbird (*Agelaius phoeniceus*, avian insectivore)
Snowy Egret (*Egretta thula*, avian piscivore)
Kingfisher (*Megacerle alcyon*, avian piscivore)
American Alligator (*Alligator mississippiensis*, reptilian predator)

The species to be sampled and analyzed for COPC residues include low- to mid-level consumers, which are forage or prey items in the food web model (crayfish, forage fish, and insects). Direct measurements of exposure to the mid- to higher-level consumers will also be obtained by sampling the frog, raccoon, little blue heron, and largemouth bass. The frog can also be considered a prey item. Eggs and nestlings (near fledging) of the prothonotary warbler will also be sampled.

A detailed characterization of the mussel community in OU-2 will be conducted. Informal observations since completion of the RI indicate that mussels are a significant component of the basin ecosystem and, as such, are an important consideration in the remedial decision for OU-2. Although not listed above as one of EPA's specified prey items in the food web model, mussels are widely reported to be important prey of many aquatic and terrestrial vertebrates, including wading birds such as herons, certain waterfowl, and mammals such as raccoons. Mussels will also be sampled and analyzed for COPC residues.

In addition to the exposure data, this revised Work Plan describes procedures for collecting additional limnological, sedimentation and hydrology data from OU-2.



RE: U.S.G.S. 7.5 MINUTE SERIES QUADRANGLE MAP, McINTOSH, ALABAMA, 1984 AND GINHOUSE ISLAND, ALABAMA, 1984.

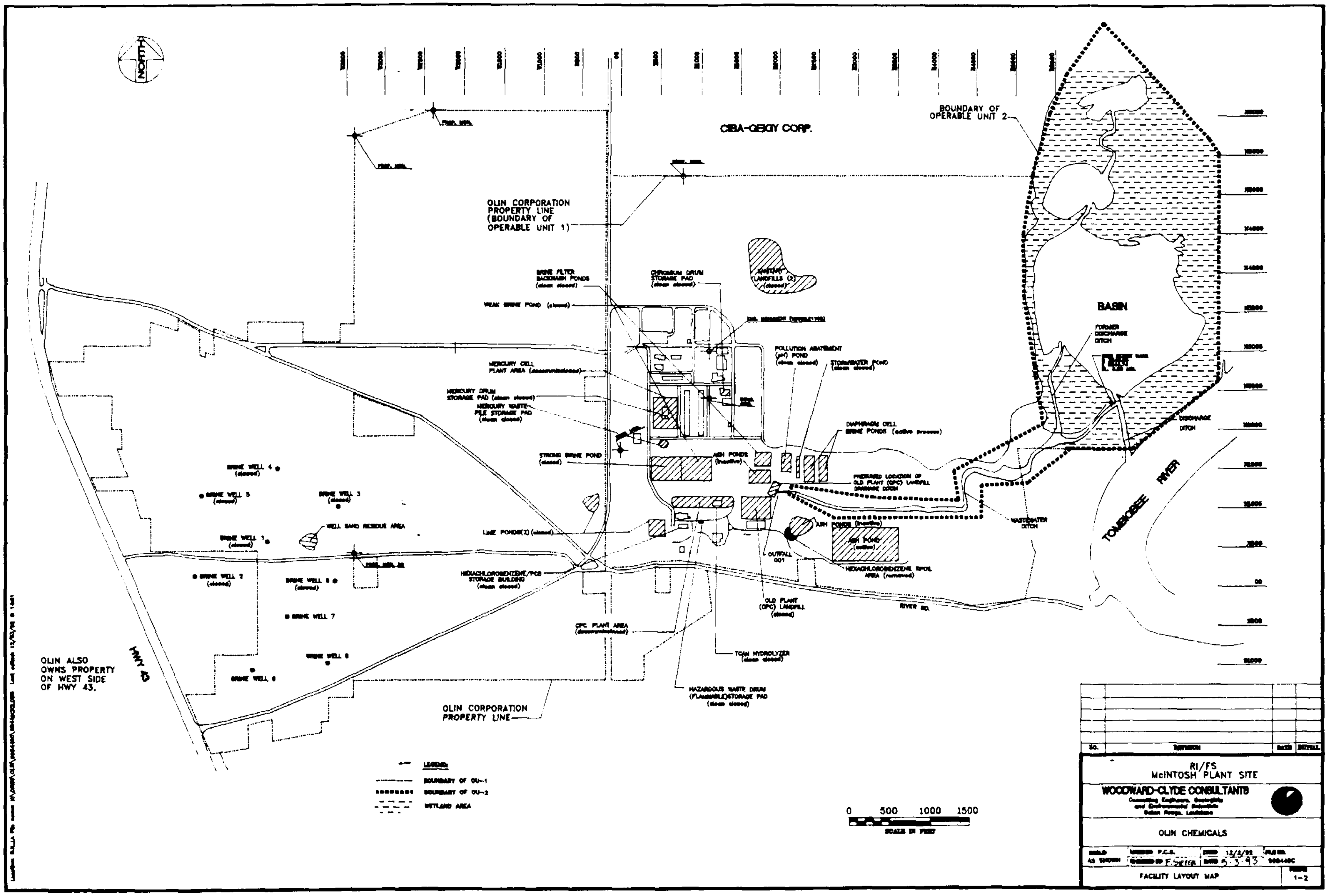
RI/FS
McINTOSH PLANT SITE

Woodward-Clyde Consultants
Consulting Engineers, Geologists
and Environmental Scientists
Baton Rouge, Louisiana

OLIN CHEMICALS

SCALE:	MADE BY: SJL	DATE: 12/90	FILE NO.
AS SHOWN	CHECKED BY: LWA	DATE: 12/7/90	90B449C

SITE LOCATION MAP FIGURE 1-1


NORTH
CIBA-GEIGY CORP.
BOUNDARY OF
OPERABLE UNIT 2
OLIN CORPORATION
PROPERTY LINE
(BOUNDARY OF
OPERABLE UNIT 1)
BRINE FILTER
BACKWASH PONDS
CHROMIUM DRUM
STORAGE PAD
SANITARY
LANDFILLS (2)
WEAK BRINE POND (closed)
BASIN
FORMER
DISCHARGE
DITCH
POLLUTION ABATEMENT
(pH) POND
STORMWATER POND
MERCURY CELL
PLANT AREA
MERCURY DRUM
STORAGE PAD
MERCURY WASTE-
PILE STORAGE PAD
DIAPHRAGM CELL
BRINE PONDS
DISCHARGE
DITCH
STRONG BRINE POND
(closed)
ASH PONDS
BRINE WELL 4
BRINE WELL 5
BRINE WELL 3
WELL SAND RESIDUE AREA
BRINE WELL 1
LIME PONDS(2)
ASH POND
OUTFALL
001
HEXACHLOROBENZENE SPOIL
AREA (removed)
WASTEWATER
DITCH
TOMBIGBEE RIVER
BRINE WELL 2
BRINE WELL 6
BRINE WELL 7
BRINE WELL 8
BRINE WELL 9
HEXACHLOROBENZENE/PCB
STORAGE BUILDING
OLD PLANT
(OPC) LANDFILL
(closed)
RIVER RD.
OPC PLANT AREA
TCAM HYDROLYZER
HAZARDOUS WASTE DRUM
STORAGE PAD
OLIN ALSO
OWNS PROPERTY
ON WEST SIDE
OF HWY 43.
HWY 43
OLIN CORPORATION
PROPERTY LINE
LEGEND:
BOUNDARY OF OU-1
BOUNDARY OF OU-2
WETLAND AREA
0 500 1000 1500
SCALE IN FEET
NO.
RI/FS
McINTOSH PLANT SITE
WOODWARD-CLYDE CONSULTANTS
OLIN CHEMICALS
AS SHOWN
P.C.G.
12/2/92
5.3.93
FACILITY LAYOUT MAP
1-2

34 0152

2.0
DATA COLLECTION PROGRAM

The objectives, approach, and rationale for the additional ecological studies of OU-2 were discussed in Section 1.0. This section summarizes the various data-gathering activities. Details of specific biological and ecological methods are presented in a series of "Protocols" included in Appendix A, or, as in the case of many of the conventional water quality analyses, will be taken directly from the standard reference documents (e.g., APHA, 1992). Table 2-1 provides an overview of the field data-gathering activities.

2.1 SELECTION OF REFERENCE AREAS

A reference area similar to OU-2 will be selected for biological and abiotic sampling and direct measurements corresponding to those in OU-2. This area is referred to herein as the primary reference area to distinguish it from several other areas (including the primary reference area) to be used in extended comparisons of mussel communities in Tombigbee River backwater habitats in the general vicinity of McIntosh.

2.1.1 Primary Reference Area

Eight candidate areas have been identified through a screening process using ARC/INFO Geographical Information System (GIS) software, inspection of various maps, and discussion with local residents knowledgeable of the area (Figure 2-1). Digital data entered into the GIS were obtained from the United States Geological Survey (USGS) Earth Science and Information Center (ESIC) in Denver. All features representing hydrology and roads were derived from 1:100,000 scale digital line graph (dlg) files. These files were compiled by the USGS from topoquads that were last updated in the 1980s. Several topoquads were linked together and the study area clipped out and scaled accordingly. Attributes such as road type were displayed through different macros constructed within the GIS. Data from the topoquads meet all national mapping accuracy standards. Data for land use and land cover (LULC) were compiled from 1:250,000 scale digital maps. These data were derived from aerial photos and

satellite imagery and were last compiled in the early 1970s. Attributes were set up on a polygon basis with each polygon containing a land use code.

The screening for selection of candidate reference areas was performed as an iterative series of queries designed to reject areas that do not satisfy the following criteria:

- Must include a pond- or lake-like water body at least 10 acres in area, which is hydrographically connected (at least seasonally) with the mainstream Tombigbee River between McIntosh and Coffeeville;

- The included water body must abut (on at least one side) a wetland, and cannot be within 1 kilometer of any "built-up" area (i.e., town, industrial facility, or major agricultural area); and

- The included water body must be within 100 meters of a road or trail.

Further considerations in the final selection of the primary reference area will include:

- Evidence that all of the organisms to be sampled have a high probability of occurring in sufficient densities to provide the requisite number of samples;

- Presence of similar vegetative cover to that present in OU-2; and

- Accessibility (i.e., verification that landowner(s) approve of use of their property as a reference area).

Final selection of the primary reference area will be accomplished by June 1, 1994. Olin plans to visually inspect seven of the candidate areas from the air. One of the areas, Hatchetigbee Lake, has already been used as a reference site in earlier phases of the RI, but experience has shown that it may not harbor freshwater mussels in sufficient abundance. Once the seven areas have been inspected from the air, they will be ranked according to size, accessibility, and other factors, and then visited in order of

priority for an on-ground inspection. Some of the sites may be eliminated prior to visitation due to considerations such as access.

2.1.2 Mussel Reference Areas

As part of the process described above, up to five backwater habitats will be retained (if accessible) for mussel surveys as described in Section 2.3 and in Protocol 4. The mussel reference areas will be selected from the candidate reference areas in Figure 2-1 with possible consideration of other areas that were not retained as candidates but may be suitable for the purpose of the mussel populations survey. Sampling of mussels for COPC analysis will be performed in a reference area where one of the species known to occur in OU-2 is available in sufficient numbers. To the extent that it contains enough mussels of the appropriate species, preference will be given to the primary reference area.

2.2 REFINING EXPOSURE ESTIMATES

The Work Plan activities are aimed at developing a clearer understanding of actual and potential exposures of ecological receptors to site-related COPCs.

2.2.1 COPCs in Abiotic Media

Additional information will be collected to assess localized concentrations of the COPCs in selected habitats of OU-2 (e.g., shallow marginal portions of the permanent water-bodies, locations from which species targeted for sampling and receptors targeted for modeling are likely to feed). Representative samples for COPCs in the primary reference area will be collected for comparison. Exact numbers and locations will be determined once the primary reference area is selected; to the extent possible, the sample locations will be comparable between study areas.

A minimum of 12 samples of surficial aquatic sediments and floodplain soils will be collected from each of the two study areas (OU-2 and the primary reference area). In each area, triplicate grabs will be collected from four separate stations in aquatic habitats and the floodplain, respectively. The sampling will follow a stratified random

design, in that the sites will be selected to represent habitats of interest (i.e., from where biological samples are expected to be collected or receptors to be modeled may feed), but the individual grabs will be taken at random within each site (Protocol 1).

At a minimum, 10 percent of the sediment and soil samples will be analyzed by analytical methods with estimated detection limits of 0.0001 mg/kg (DDTr) to 0.001 mg/kg (Hg). The analytical methods are discussed in Section 2.6 and Protocol 2.

A minimum of six water samples will be collected from near the surface in aquatic habitats of each study area. These samples will be collected at the beginning of the sampling activities. Sampling locations will be selected to represent the various major types of aquatic habitats available. These locations will coincide with those used for sampling/measurement of "conventional" water quality parameters (see Section 2.4). Two locations in OU-2 will be in the two smaller water-bodies to the north of the Basin.

At a minimum, 10 percent of the water samples will be analyzed by analytical methods with estimated detection limits of 0.00001 µg/l (Hg) to 0.002 µg/l (HCB). The analytical methods are discussed in Section 2.6 and Protocol 2.

2.2.2 COPC Residues in Biological Media

Additional data will be collected on the concentrations of COPC residues in the tissues of representative organisms. Three general categories of organisms are planned to be sampled: (1) mid- to higher-level consumers representing four vertebrate classes; (2) producers and low- to mid-level consumers which are expected to serve as forage or prey for higher-level consumers; and (3) nestlings of birds. Sampling for COPC residues in biological media is summarized below and described in more detail in Protocol 3. The biological tissue analytical methods are described in Protocol 2. A minimum of six samples of each species will be collected from OU-2 and the reference to provide a statistical basis for distinguishing differences between the two areas. (See Section 4.1 for a discussion of the statistics). The actual number of samples per species, which is commonly more than six, is also based on the number judged to be representative and the expected availability, i.e., number of animals likely to exist in an area the size of OU-2 or the reference."

2.2.2.1 Higher-Level Consumers

The four mid- to higher-level consumers to be sampled are the largemouth bass (*Micropterus salmoides*); the bullfrog (*Rana catesbiaena*); the little blue heron (*Egretta caerulea*); and the raccoon (*Procyon lotor*). From previous observations, each is known to be relatively abundant in OU-2 and can be expected to occur in similar densities in comparable reference areas. With the exception of the little blue heron (LBH), there is a substantial body of scientific (including ecotoxicological) literature on these species.

In addition to the whole body analysis, selected tissues (i.e., feathers and hair) of the two warm-blooded vertebrates, LBH and raccoon, may be sampled to evaluate the possibility of establishing a relationship between COPC residues in the whole body, and feathers or hair, respectively. If such a relationship can be clearly defined, it will be possible to sample these species non-destructively as part of long-term monitoring.

2.2.2.2 Forage/Prey Organisms

Producers and low- to mid-level consumers which are potentially important forage or prey organisms in the OU-2 ecosystem that will be sampled include mussels, crayfish, mosquitofish and terrestrial stages of insects.

Both mussels and clams are widely-recognized as important prey for many vertebrates, including the raccoon and wading birds such as the little blue heron. Intensive mussel population surveys are scheduled as described in Section 2.3, because of the importance of these animals as indicators of pollutant-related stress (Foster, 1974; Foster and Bates, 1978). Specimens for COPC analysis will be taken in conjunction with this effort.

Crayfish are another type of prey of widely-recognized dietary significance, not only to fishes but also to the raccoon and wading birds (Lowery, 1974; DeGraaf and Rudis, 1986).

Based on preliminary observations, the mosquitofish (*Gambusia affinis*) is expected to be a key prey item for wading birds and many other terrestrial, amphibious, and aquatic animals.

Terrestrial stages of insects are widely recognized as the main prey of numerous birds, such as the prothonotary warbler. These insects also contribute significantly to the diets of many other mid- to higher-level consumers (e.g., frogs and other "herptiles," small mammals).

2.2.2.3 Bird Nestlings

Eggs and nestlings (near fledging) of prothonotary warblers (*Protonatoria citrea*) will be sampled from artificial nesting enclosures (Protocol 3). Six eggs and six nestlings will be collected for analysis of whole body COPC residues from both OU-2 and the reference area.

2.3 MUSSEL POPULATION STUDIES

Intensive mussel population surveys will be conducted as outlined in Protocol 4. Freshwater mussels are bivalve mollusks (similar to clams) of the Family Unionidae. Several mussels are believed to be extinct, and many others are federally-protected as endangered or threatened. For example, the recently-issued recovery plan for the threatened inflated heelsplitter (*Potamilus inflatus*) indicates that the species may occur in the McIntosh area.

Mussels are relatively long-lived, compared to most other freshwater organisms, and are sedentary, living in close association with sediments, and feeding primarily by filtering fine particulate organic matter. Consequently, mussels are considered to be particularly vulnerable to sediment-adsorbed contaminants and are widely used in biomonitoring. Where abundant, mussels are important prey for numerous higher-level consumers, such as fish, wading birds, and mammals.

The planned mussel population studies described in this revised Work Plan will include an estimated three to five reference areas depending on availability of similar floodplain habitats, and access. The use of this number of reference areas is intended to provide a more thorough understanding of mussel diversity and distribution in the region than would have been afforded by comparison with only the primary reference area. As designated for the other biological media, tissue residue data for the mussels will be

collected from OU-2 and one reference area. It is anticipated that the mussels sampled for COPC analyses will be collected from the primary reference area as described in Section 2.2.2, although this will be dependent on the availability of mussels of the same species in the primary reference area.

2.4 PHYSIOCHEMICAL LIMNOLOGY

Physicochemical limnological data will be collected to improve the understanding of spatio-temporal variation in water quality throughout OU-2 using the methods outlined in Table 2-2 and Protocol 5. In OU-2 and the reference area, six locations will be visited twice, once at the beginning of the sampling program and once at the end, to obtain *in situ* measurements or samples for subsequent analyses of 11 characteristics. The "classical" limnological attributes such as temperature, dissolved oxygen, pH, specific conductance, hardness, alkalinity, are included. In addition several characteristics of relevance to COPC fate and transport will be measured, such as suspended solids, sulfate, total organic carbon, and oxidation/reduction (redox) potential. At the six locations, Ekman grab samples will be taken of sediments during both sampling events for total organic carbon (TOC) analyses and sediment particle size.

2.5 SEDIMENTATION AND HYDROLOGY

Results of hydrodynamic studies completed during the RI strongly suggest that OU-2 is fundamentally a depositional area and that turbulence, even under flooding conditions, is seldom, if ever, high enough to cause significant erosion of the sediments. Additional measurements will be obtained under this revised Work Plan as described in detail in Protocol 6. Continuously-recording devices will monitor both direction and velocity of currents at strategic locations in OU-2. One meter will be deployed along the eastern portion of the basin. This is judged to be the critical area to monitor potential river flow across the levee or across the northern boundaries of the basin during high river stages. A second meter will be deployed near the weir at the south end of the basin to monitor currents during storm events. In addition, simple devices will be deployed at 16 "sites" to measure sedimentation (or erosion) rates (Protocol 6). The resulting data will provide information on natural rates of accumulation or depletion of sediments in the system for interpreting future bioavailability of the COPCs.

2.6 LABORATORY ANALYSIS

Table 2-3 summarizes the analytical methods and detection limits for the COPC analyses. Table 2-2 summarizes the planned analytical methods for water quality parameters.

This revised Work Plan provides for analysis of a subset of soil/sediment and water samples using low detection limit methods. Protocol 2 includes proposed methods for these analyses. However, Olin has requested that EPA provide guidance on the methods acceptable to EPA and Olin is continuing to evaluate the available methods. Any modification to the methods described in Protocol 2 would be submitted to EPA for their approval prior to sampling.

2.6.1 Sample Preservation and Holding Times

Soil and sediment samples for HCB and DDTr will be placed in 8-oz/250 ml, wide-mouth solvent-cleaned glass jars with Teflon®-lined screw tops. Water samples for HCB and DDTr analyses will be placed in four liter amber solvent-cleaned glass bottles with Teflon®-lined screw tops. The soil/sediment samples for mercury analyses will be placed in laboratory-cleaned 125 ml or 250 ml Teflon® jars. The water samples for mercury analyses will be placed in laboratory-cleaned 60 ml glass jars with Teflon®-line screw tops or 60 ml polyethylene jars. The soil, sediment and water samples will be shipped from the site to the contract laboratory at approximately 4° C in coolers containing ice.

Biological tissue samples will be wrapped in aluminum foil (shiny side out) and/or placed in sealed plastic bags and shipped from the field in coolers containing ice (at approximately 4° C) to the WCC laboratory in Franklin, Tennessee. Tissue samples will be stored, protected from light and frozen at approximately -20°C from the time of receipt in the laboratory until sample preparation. Tissue sample preparation procedures, consisting of grinding and homogenization, are discussed in Protocol 3. The homogenized tissue samples will then be placed in glass jars with Teflon®-lined screw tops, and shipped to Hazleton Environmental Services for the COPC analyses.

Sample preservation and sample holding times for the COPC analyses are summarized below:

Parameter/Matrix	Preservation	Holding Time
Water		
Mercury	Cool 4° C[1]	28 days of collection
Hexachlorobenzene	Cool 4° C	7 days of collection
4,4'-DDT		40 days of extraction
4,4'-DDE		
4,4'-DDD		
Soil/Sediment		
Mercury	Cool 4° C	28 days of collection
Hexachlorobenzene	Cool 4° C	14 days of collection[2]
4,4'-DDT		40 days of extraction
4,4'-DDE		
4,4'-DDD		
Biological Tissue	Cool 4° C for shipment Store in laboratory frozen at -20° C	No established holding times

1 Bromine monochloride will be added by the laboratory within 24 hours of receipt.
2 Can be held longer if frozen

Holding times for the water quality parameters will be as specified by the selected analytical method.

2.6.2 Quality Control

The quality control analyses for the COPCs will include method blanks, duplicates and matrix spikes. The quality control analyses for hexachlorobenzene and DDTr will also include surrogates. At a minimum, a method blank will be processed each time 20 or fewer samples are prepared or a new source of reagent is utilized. A laboratory matrix spike and matrix spike duplicate or duplicate, as specified in the appropriate analytical method, will be analyzed for each group of 20 or fewer field samples.

Quality control analyses and control limits for the water quality parameters will be as specified by the selected analytical method.

2.6.3 Reporting

The final analytical reports for the COPC analyses will include the following:

- Case Narrative
- Chain-of-Custody
- Quality Control Summary
- Sample Data Summary
- Calibration
- Raw Sample Data
- Raw Quality Control Data
- Sample Preparation Logs
- Instrument Run Logs

The raw analytical data will consist of analytical bench sheets and/or instrument print outs.

2.6.4 Data Validation and Review

The data will be evaluated for completeness and conformance with the specified protocols.

The chain-of-custody documents will be reviewed for completeness and correctness.

The analytical data will be reviewed at a frequency of approximately 10 percent for the following areas:

- Sample holding times
- Calibration
- Blanks
- Surrogate recovery as appropriate with the specified protocol
- Laboratory control samples as appropriate with the specified protocols
- Matrix spikes/matrix spike duplicates or duplicates
- Analyte identifications

- Analyte quantifications
- System performance
- Overall assessment of data for a case
- Documentation

A data summary will be prepared following data validation and will include the following:

- Sample identification
- Validated sample results
- Sample matrix
- Proper concentration units
- Proper number of significant figures

This data summary will be reviewed for potential data quality problems including:

- Common laboratory contaminants
- Unusual spacial concentrations/identification relationships
- Unexpected results

The results of the data review will be summarized in a brief written report.

3 4 0160

TABLE 2-1

SUMMARY OF FIELD EFFORT - ADDITIONAL ECOLOGICAL STUDIES OF OU-2

Activity	Samples[1] per Area		Total Samples	Protocol(s) Appendix A[2]
	OU-2	Reference		
COPC ANALYSES				
Ecological Chemicals of Potential Concern (COPC) Concentrations in Sediment	12	12	24	1, 2
COPC Concentrations in Soil	12	12	24	1, 2
COPC Concentrations in Water	6	6	12	1, 2
Whole Body (WB) COPC Residues in Raccoon	6	6	12	2, 3
COPC Residues in Raccoon Hair	6	6	12	2, 3
WB COPC Residues in Little Blue Heron (LBH)	9	9	18	2, 3
COPC Residues in LBH Feathers	9	9	18	2, 3
COPC Residues in Nestlings of Prothonotary Warbler	6	6	12	2, 3
COPC Residues in Eggs of Prothonotary Warbler	6	6	12	2, 3
WB COPC Residues in Crayfish	12	12	24	2, 3
WB COPC Residues in Mussel	12	12	24	2, 3, 4
WB COPC Residues in Mosquitofish	12	12	24	2, 3
WB COPC Residues in Largemouth Bass	9	9	18	2, 3
COPC Residues in Terrestrial Insects	12	12	24	2, 3
COPC Residues in Bullfrogs	12	12	24	2, 3
"Subtotal" COPC Analyses			282	
MUSSEL POPULATION STUDIES				
Mussel Survey (ID/Count/Measure, etc.)	3	3[4]	N/A	4
PHYSIOCHEMICAL LIMNOLOGY STUDIES				
11 Water Quality Parameters	12[3]	12[3]	24	5
TOC in Sediment	12[3]	12[3]	24	5
Particle Size	12[3]	12[3]	24	5
SEDIMENTATION AND HYDROLOGY STUDIES				
Sedimentation Studies	16		N/A	6
Current Measurements (Continuous)	2		N/A	6

NOTES:

1. "Samples" denotes observations (measurements) as well as items; actual samples may be discrete or composite depending upon medium.
2. Protocols in Appendix A contain the detailed methods for performing the activities.
3. Six samples collected from each study area twice during the sampling program.
4. Mussel population studies are planned for three to five reference areas.

TABLE 2-2

WATER QUALITY PARAMETERS AND METHODS[1]

Chemical Parameter	U.S. EPA Method or Equivalent[1]	Laboratory or Field Test
Oxidation-Reduction	ASTM D1498-76 (1981)	Field
Dissolved Oxygen (mg/l)	360.1	Field
Temperature (°C)	170.1	Field
pH (Std. units)	150.1	Field
Light Transmission (Secchi)	N/A	Field
Specific Conductance Conductivity (μMho/cm)	120.1	Field
Sulfate (mg/l)	375.1, 375.3 or 375.4	Laboratory
Hardness as $CaCO_3$ (mg/l)	Std. Methods 2340.B[2]	Laboratory
Total Alkalinity (mg/l)	310.1	Laboratory
Total Suspended Solids (mg/l)	160.2 or Std. Methods 2540D[2]	Laboratory
Total Organic Carbon (mg/l)	415.1	Laboratory

NOTES:

1 Unless otherwise indicated, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (Revised March 1983), Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, OH, 1979.

2 Standard Methods for the Examination of Water and Wastewater, Seventeenth Edition, American Public Health Association, Washington, D.C., 1989.

TABLE 2-3

SUMMARY OF ANALYTICAL METHODS

BIOLOGICAL TISSUE

Parameter	Method[1]	Estimated Method[2, 3] Detection Limit (mg/kg)
Mercury	MP-HGE-MA	0.025
Hexachlorobenzene	MP-FWST-MA	0.01
4,4' - DDT	MP-FWST-MA	0.01
4,4' - DDD	MP-FWST-MA	0.01
4,4' - DDE	MP-FWST-MA	0.01

WATER

Parameter	Method	Estimated Method[3] Detection Limit (µg/l)
Mercury	Cold Vapor Atomic Fluorescence[4]	0.00001
Hexachlorobenzene	Modified SW-846[5] Method 8080	0.002
4,4' - DDT	Modified SW-846[5] Method 8080	0.001
4,4' - DDD	Modified SW-846[5] Method 8080	0.001
4,4' - DDE	Modified SW-846[5] Method 8080	0.001

TABLE 2-3 (Continued)

SUMMARY OF ANALYTICAL METHODS

SOIL/SEDIMENT (HAZLETON METHODS)

Parameter	Method[1]	Estimated Method[3] Detection Limit (mg/kg)
Mercury	MP-HGE-MA	0.025
Hexachlorobenzene	MP-FWSS-MA	0.01
4,4' - DDT	MP-FWSS-MA	0.01
4,4' - DDD	MP-FWSS-MA	0.01
4,4' - DDE	MP-FWSS-MA	0.01

SOIL/SEDIMENT (LOW DETECTION - LIMIT METHODS)

Parameter	Method[1]	Estimated Method[3] Detection Limit (mg/kg)
Mercury	Cold Vapor Atomic Fluorescence[4]	0.001
Hexachlorobenzene	Modified SW-846 Method 8080[5]	0.0005
4,4' - DDT	Modified SW-846 Method 8080[5]	0.0001
4,4' - DDD	Modified SW-846 Method 8080[5]	0.0001
4,4' - DDE	Modified SW-846 Method 8080[5]	0.0001

TABLE 2-3 (Continued)

SUMMARY OF ANALYTICAL METHODS

NOTES:

DDT and its metabolites DDD and DDE will be reported as the sum of 4,4'-DDT, 4,4'-DDD, and 4,4'-DDE, and labeled as DDT.

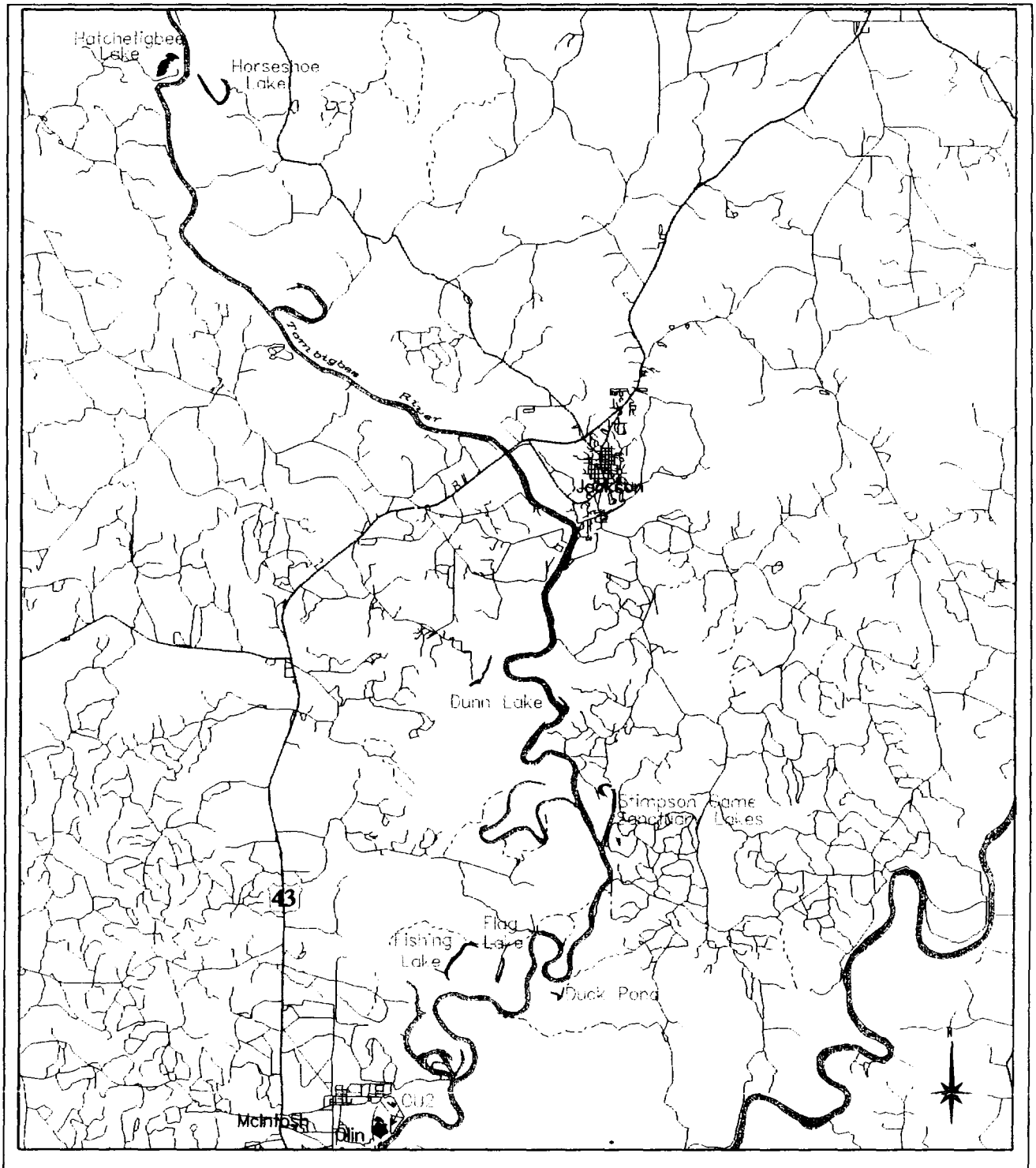
[1] These analyses are planned to be conducted by Hazleton Environmental Services in Madison Wisconsin. The planned analytical methods developed by Hazleton are presented in Appendix A, Protocol 3.

[2] For the biological tissue analyses, the detection limits indicated are based on a minimum sample size of 2 grams for the mercury analyses and 5 grams for the hexachlorobenzene and DDTr analyses. These samples sizes may not be attainable for some of the tissues, which would result in elevated detection limits.

[3] Elevated detection limits could occur for those samples exhibiting high analyte concentration levels and/or interferences.

[4] Method performed by Frontier Geosciences of Seattle, Washington described in Appendix A, Protocol 3.

[5] Method Performed by Battelle Marine Sciences Laboratory of Sequim, Washington described in Appendix A, Protocol 3.



McINTOSH PLANT SITE

Olin CHEMICALS

CHARLESTON, TENNESSEE

Woodward-Clyde

Engineering and sciences applied to the earth and its environment

Franklin, Tennessee

SCALE:	DRAWN BY: G. DANIELS	DATE: 05/11/94
1" = 2.5 mi	CHKD. BY: J. CONNER	DATE: 05/11/94

CANDIDATE REFERENCE AREAS SELECTED BY GIS SCREENING FOR ADDITIONAL ECOLOGICAL STUDIES

- AREAS MEETING CRITERIA
- PRIMARY ROADS
- SECONDARY ROADS
- TERTIARY ROADS
- TRAILS

FILE NO. 93N063C

FIG. NO. 2-1

3.0
SAMPLE DOCUMENTATION AND DATA MANAGEMENT

3.1 FIELD ACTIVITIES DOCUMENTATION

All information pertinent to field observations and sampling will be recorded in a bound field logbook with consecutively numbered pages. All entries in the field log book will be made in ink; no erasures will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark and initialed. General information recorded in the log book will include:

- Date
- WCC project name and number
- Members of the sampling crew and any other personnel observing the sampling
- Location and sampling activity and address
- Weather conditions
- Any deviation from the procedures outlined in the work plan

The documentation in the log book will be sufficient to reconstruct the sampling situation without relying on the collector's memory.

More details of the information that will be recorded for the specific sampling activities are described in the protocols in Appendix A.

3.2 SAMPLE DESIGNATION AND LABELING

All samples will be identified by a unique sample designation, which will be established as follows: sample matrix abbreviation/location designation (i.e., OU-2, Reference Area)/site designation and replicate number. For example, the first water sample collected from location G4 in OU-2 may be labeled WTO2G41. The third largemouth bass sample collected during the first electrofishing run in Reference Area 1 may be labeled LBR1E11.

Labels will be used for sample security, identification, and integrity. Information on the sample container will include the following:

- WCC project number
- Sample designation number
- Date and time of sample collection
- Designation of the sample as a grab or composite
- The initials of the sampler(s)
- Whether the sample is preserved
- Any other relevant comments

3.3 SAMPLE CONTAINMENT AND SECURITY

Samples will be stored in a manner that will not jeopardize the representativeness of the media sampled. For samples to be analyzed for chemical parameters (e.g., water, sediment, fish samples, etc.), normally this will mean freezing or storage on ice or refrigeration, in closed containers. Samples will be analyzed within the holding times stated in the analytical procedures discussed in Section 2.6.

Sample coolers will be under the direct observation of WCC personnel at all times or secured with custody seals to detect tampering. If samples are not attended, they will be kept in a secured facility. All samples will be turned over to the WCC field operations task leader or his designee at the end of the day, along with chain-of-custody forms and field documentation forms. Samples placed in the coolers will be packed with ice or ice packs upon retrieval and will be maintained at approximately 4°C until delivery to the laboratory. Prior to shipment, a second person (other than the one packing the cooler) will verify samples, chain-of-custody and other documentation.

3.4 CHAIN-OF-CUSTODY PROCEDURES

Chain-of-custody procedures for each sample will be documented from the time the sample is taken until it reaches the laboratory. A chain-of-custody form will be initiated in the field, and the original will accompany the samples with copies retained at intermediate steps. The chain-of-custody form will be signed by the sample custodian.

It will be placed in a water-tight plastic bag and taped to the underside of the lid of the cooler containing the samples designated on the form. The lid of the cooler will be securely taped shut with custody seals, using evidence tape to allow detection of any possible tampering. Upon arrival in the laboratory, samples will be received by the analytical laboratory representative. Samples contained in the shipment will be compared to the chain-of-custody form to ensure that all samples designated have been received. Sample custody within the laboratory will be maintained on internal tracking forms.

Each time responsibility for custody of the sample changes, the new custodian will sign the record and denote the date. An exception would be the commercial carrier, if used. A copy of the signed record will be made and retained by the immediately previous custodian and sent to the designated WCC personnel to allow tracking of sample possession. All changes of custody of samples must be a person-to-person change of physical possession.

3.5 DATA MANAGEMENT

A database system has been developed for the site and includes the historical RCRA groundwater sampling data and the data collected for the RI/FS. The analytical and field data collected for this investigation will be input into this database.

The field data will be entered from the field log book or field data sheets. As each set of analytical data are validated, as described in Section 2.6.4, the results will be entered or transferred to the database. The data will be stored by type/matrix (i.e., fish, water, sediment, etc.), analytical or field parameter, identification number (i.e., sample I.D.) location, matrix and any other attributes specific to the parameter or matrix. This system enables retrieval of information specific to various interests since it will be input into various fields (as described above). The data will be referenced to location, so it can be transferred directly into the geographical information system (GIS) as described in Section 4.3.

4.0
DATA REDUCTION AND EVALUATION

This section describes the data reduction and evaluation techniques that will be employed.

4.1 STATISTICAL METHODS

The sampling programs described in Section 2.0 are designed to be balanced (i.e., there are the same number of samples in OU-2 as the reference area).

The purpose of the statistical tests described in this section is to evaluate the differences between the site and the primary reference area. Basic statistical tests for differences between means (paired t-tests) as well as tests such as analysis of covariance will be employed. The degree to which differences between and within sites can be detected will be controlled by the variance of the data. An alpha value of 0.95 and a beta value of 0.80 will be used in all statistical analysis (i.e., 95 percent confident that differences between means are true 80 percent of the time). A beta value of 0.80 is increasingly used for analysis of biological data in the environmental field (Green and Young, 1993). Assuming the sample variance is 100 percent or less, the sampling designs will allow for the detection of at least four-fold differences in means employing standard two-sided t-tests. Table 4-1 shows k-fold differences in means that can be detected by a two-sided t-test for a given number of samples of different variances.

In the statistical analysis, the data will first be subjected to plotting routines and the w-test to assess sample distribution. If the data are not from a randomly distributed population then attempts will be made to transform the data to a normal distribution prior to employing parametric protocols (for example, lognormal transformation). If data transformation does not normalize the data, then non-parametric statistical procedures will be used.

4.2 FOOD CHAIN MODELING

Food chain modeling provides a means by which future receptor exposures or body burdens are projected to assess, directly or indirectly, the potential effect of reasonable future conditions or remedial actions. A dietary exposure model will be used, such as that presented in the RI report (WCC, 1993) to assess exposures. Site-specific tissue concentrations of the prey items will be input. Information from the literature will be used to estimate model components such as the percent of forage/prey items in the diet, site foraging frequency, food ingestion rate, and body weight. The model components (exposure assumptions) will be submitted to EPA for its review and approval prior to using the model. The dietary exposure model is described in detail in the RI report and is incorporated into this revised Work Plan by reference.

A mass-balance modeling approach will also be investigated for possible application at the site. In simplest terms, this model will provide a mathematical framework for projecting COPC concentrations (and body burdens) in several receptors at various trophic levels based on COPC concentrations in various environmental media. The uptake and loss of a COPC in receptor organisms will be expressed mathematically to assess the body concentration or body burden at a selected point in time. These models will be inter-related in that the output generated for lower-level (prey) species will be used as input into the higher level (predator) receptor models, thus resulting in a food-chain modeling approach. The model theory and approach are discussed in the following sections.

4.2.1 Model Theory

The concentration of COPCs in aquatic organisms is dependent on several physical, chemical and biological factors. These factors act to enhance or retard concentration gradients between organisms and their environmental matrix in both spacial and temporal dimensions. For DDTr, HCB and mercury, some of these physical factors are known.

For example, since DDTr and HCB are nonionic they do not easily form hydrogen bonds with water molecules and thus have an extremely low solubility in pure water.

Therefore, when introduced into the aquatic environment, they readily partition through association with lipophilic substances or sorption to mineral sediments and suspended material. This characteristic results in a very large partition between the concentration of DDTr and HCB in water and sediment materials. Sediments may then be described as "sinks" because they tend to remove COPCs from the water phase. Consequently, sediments contain the greatest mass of COPCs in the aquatic environment. In the natural environment, sediment-water-COPC interactions exist in a state of dynamic balance rather than true equilibrium.

Unfortunately, the tendency for sediments to concentrate DDTr, HCB and mercury ultimately results in sediments becoming a long-term "source" for COPC contamination to aquatic organisms. To assess the levels of COPCs in aquatic sediments that will result in unacceptable concentrations in a particular receptor (e.g., fish) species requires a thorough knowledge of sediment-water-COPC interaction as well as knowledge of how COPCs are accumulated (and eliminated) by the fish and its food organisms.

The interactions of COPCs with the chemical, physical, and biological processes within an aquatic system are complex and site-dependent. Therefore, to make environmentally sound and cost-effective decisions concerning mitigative alternatives, data specific to controlling the mass movement of COPCs between the sediments and fish species at the Olin basin is of primary importance. Figure 4-1 presents a compartmental model that shows the pathways of COPC exchange among the biotic and abiotic components of the aquatic environment and the kinetic and equilibrium constants that control the distribution of COPCs between compartments.

In general terms, the bioaccumulation of a substance in an organism is the sum of uptake and loss of the substance. Uptake can occur through contact or ingestion. Loss, commonly known as depuration, occurs through excretion. To understand the processes involved in controlling the uptake and loss of COPCs by fish, simplistic kinetic models have proven to be useful tools (Pentreath, 1973; Branson et al., 1975; Krzeminski et al., 1977; Veith et al., 1979; Thomann, 1981; Wilson, 1978).

For example, consider a finite column of water (i.e., a "compartment" of water) that covers a uniform deposit of COPC-contaminated sediment. The compartment receives

and releases water, i.e., flow. The COPC concentration in the water compartment can be calculated using a mass balance equation that consists of the flow and concentration of the COPC entering the compartment plus the addition (or loss) of the COPC to the water column from the sediment. Integrated over time, the mathematical form is shown below:

$$\frac{dC_w}{dt} = \frac{C_{in}-C_w}{t_o} + \frac{J_s}{Z} \quad (1)$$

where:

C_w = COPC concentration in water in the compartment
C_{in} = COPC concentration in water in the influent
t = time
t_o = hydraulic retention time
J_s = mass of COPC being released from the sediment per unit area and time calculated, for example, using partitioning coefficients.
Z = depth of water column

A fish confined to the same water compartment can assimilate the COPC directly from the water column and through the ingestion of food items in the compartment. The sum of the uptake minus the loss of the material through excretion processes results in a mass balance equation for the rate of accumulation of the total COPC body burden which may be expressed as follows:

$$\frac{dC_f}{dt} = k_w C_w W + \alpha R C_F W - k_d C_f \quad (2)$$

where:

C_f = COPC concentration in fish (μg/g)
k_w = uptake rate constant for a specific COPC (mL/g/day)
α = food assimilation efficiency (μg food absorbed divided by μg food ingested)
W = body weight
k_F = uptake rate constant from food ingestion (day^{-1})
C_F = concentration of COPC in the food organisms (μg/g)
k_d = depuration (loss) rate constant (day^{-1})
R = ration

The mechanism of COPC loss, commonly referred to as the depuration, becomes important when attempting to predict concentrations in fish. Fish ultimately attain a steady state concentration when the rate of uptake equals the rate of depuration. The steady-state concentration divided by the concentration of the constituent in water is used to describe the bioconcentration factor (BCF) in fish.

To account for the effect of the size of fish, Wilson (1978) used a correlation between the rate of uptake or depuration and the weight of fish. He replaced the rate terms such as $k_w C_F$, $k_F C_F$, and k_d, in the equation similar to Equation 2 with correlation relationships. Another approach to account for the size of fish is the use of the growth rate concept by adding a growth rate constant (day^{-1}) to the depuration constant.

4.2.2 Model Application

The mass-balance approach discussed above is presented as an example and is not proposed to be exact or inclusive of all variables that affect COPC concentrations in receptor organisms. The purpose is to show that COPC uptake and depuration can be expressed as numerical coefficients in a model formulation. As a supplement to the dietary exposure model, the mass-balance model will be examined as a potential tool for projecting key receptor COPC concentrations under reasonable future scenarios and for testing various remedial actions. Though fish were used as an example in the preceding discussion, this mass-balance model is applicable to all ecological receptors. The field activities will develop information that will be used to calibrate each receptor model. For example, the necessary inputs to the general model are presented in Equation 2 in Section 4.2.1. Inputs such as the COPC concentration in water and prey items (forage fish, crayfish earthworms and plant foliage/fruit) will be measured directly or derived from site-specific data collected in the field. Food intake and assimilation efficiency and the initial uptake and depuration rate constants will be obtained from the literature and adjusted to calibrate the model based on site-specific COPC concentrations in key receptors measured in the field. As discussed previously, the individual receptor models will be inter-related in that the output generated for lower-level (prey) species will be used as input into the higher level (predator) receptor models, thus resulting in a food-chain modeling approach. Model output will be

compared to COPC effect levels (based on body concentrations or body burdens) as derived from site-specific data collected from the site.

4.2.3 Other Considerations

If data show that the food source (C_F) is the dominant pathway for COPC accumulation then the proposed study should provide adequate information to satisfy the objectives. If uptake from the water is shown to be a significant source then the data may have to be coupled with hydraulic models (such as Equation 1, or a more sophisticated model) specific to OU-2 in order to predict COPC accumulation in fish. In the latter case, if the sediment contributes significant amounts of COPCs to the water column, then site specific hydrodynamic conditions, i.e., the water depth over the sediments and the flow rates over the sediments must also be modeled. Evaluation of more detailed kinetic models (e.g., Thomann, 1981), can provide further refinement of information needs and predictions of how environmental parameters affect COPC accumulation in fish. Whether ultimately employed as a tool for predicting COPC accumulation or not, these mechanistic modeling considerations are essential to producing data of the high scientific quality necessary to achieving the study objectives.

4.3 GEOGRAPHICAL INFORMATION SYSTEMS (GIS) APPLICATIONS

As discussed in Section 3.5, the data collected during this investigation will be entered into the existing database. Each sample collection/observation location will be referenced to the State Plane Coordinate System, and can be directly transferred from the database to the GIS system. GIS provides a powerful tool to analyze spatially related data. It is anticipated that the GIS will be used in this investigation to: (1) help locate sample reference areas (See Section 2.1); (2) show the distribution of habitat for species of concern and the distribution of COPCs within that habitat; (3) model the sedimentation occurring within the Olin basin; (4) provide the necessary descriptive mapping during the study.

TABLE 4-1

STATISTICAL DETERMINATION OF MINIMUM SAMPLE SIZE[1]

k	Coefficient of Variation									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
2	2	2	3	6	9	12	16	21	27	33
3	2	2	2	3	4	5	7	9	11	13
4	2	2	2	2	3	3	4	6	7	9
5	2	2	2	2	2	3	3	4	5	7
6	2	2	2	2	2	2	3	4	4	5
7	2	2	2	2	2	2	3	3	4	5
8	2	2	2	2	2	2	2	3	3	4
9	2	2	2	2	2	2	2	3	3	4
10	2	2	2	2	2	2	2	2	3	3
Note: Values less than 2 are rounded up to 2										

[1] **MINIMUM SAMPLE SIZE NECESSARY TO DETECT A k-FOLD INCREASE IN MEAN CONCENTRATION WITH 80 PERCENT CONFIDENCE WITH A TWO-SIDED T-TEST AT SIGNIFICANCE LEVEL 0.05 (Northeast U.S. Marine Sediments, NOAA Tech. Report No. 99)**

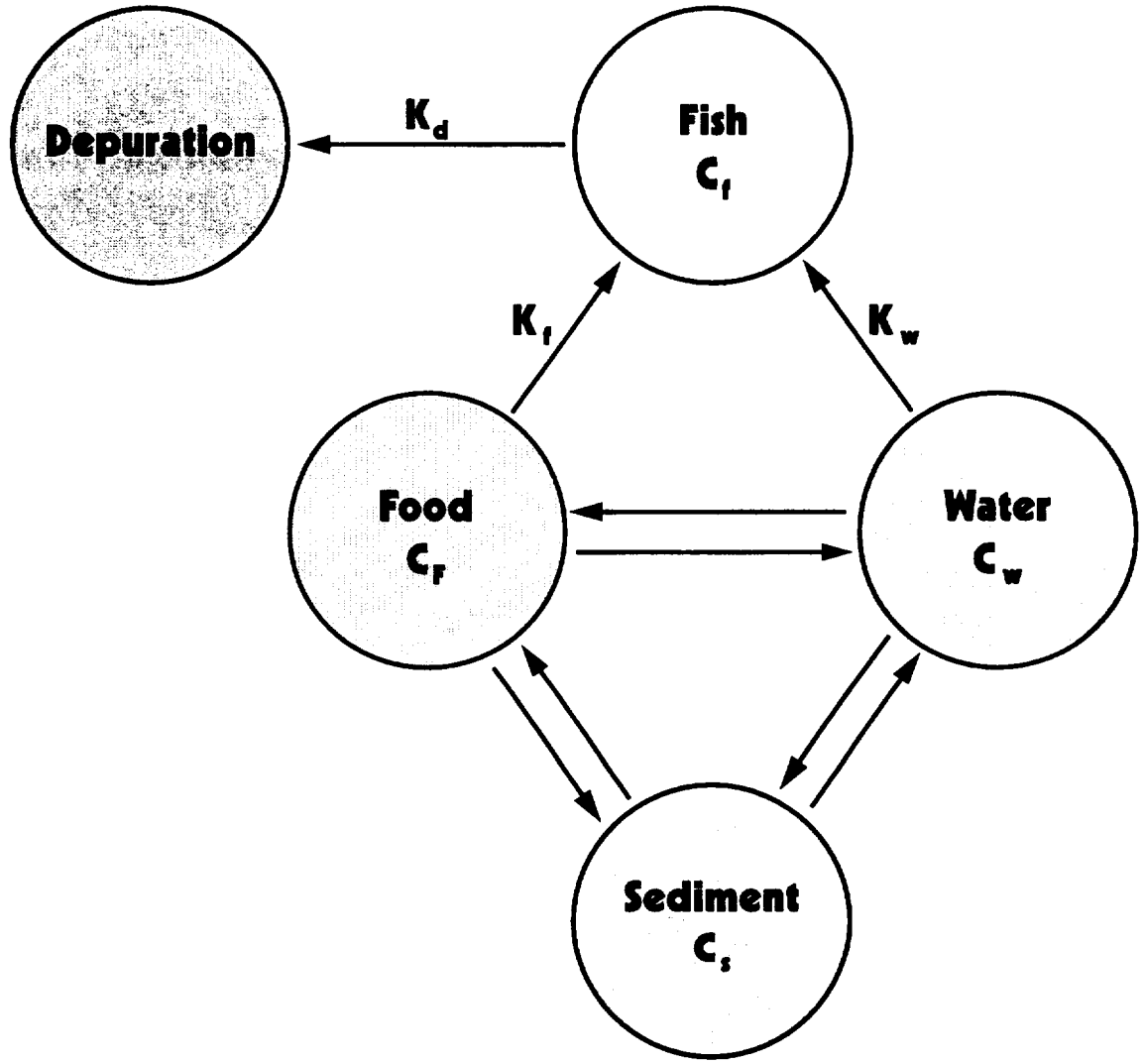


Figure 5-1. Compartment Model Showing Pathways of COPC Exchange in the Aquatic Environment, where C_f = concentration in fish, C_s = concentration in sediment, C_w = concentration in water, C_F = concentration in food source for fish.

WCC FILE #02-OLIN

McINTOSH PLANT SITE Olin CHEMICALS CHARLESTON, TENNESSEE	**Woodward-Clyde** Engineering & sciences applied to the earth & its environment **Baton Rouge, Louisiana**			COMPARTMENT MODEL SHOWING PATHWAYS OF COPC EXCHANGE IN THE AQUATIC ENVIRONMENT	FILE NO. 93N063C FIG. NO. 4-1
	SCALE: N/A	DRAWN BY: D.OLSON CHKD. BY: W.BEAL	DATE: 05/11/94 DATE: 05/11/94		

5.0
FINAL REPORT

Following data reduction and evaluation, a final report of the additional ecological studies of OU-2 will be prepared and submitted to EPA. The results of the COPC tests and other studies will be presented along with the results of the food chain modeling described in Section 4.2. These results should provide EPA with the information it has stated is required to decide if remedial action is necessary based on ecological considerations.

6.0
SCHEDULE

Figure 6-1 shows the planned schedule for the ecological studies described in this Work Plan. This schedule is based on EPA approval of the plan by June 15, 1994, with data collection activities to begin shortly thereafter. The field activities should be completed by August 13, 1994. It is anticipated that data reduction and evaluation (i.e., data validation, statistical analyses, food chain modeling, etc.) will be completed and the report submitted on October 28, 1994.

Because some of the activities are not completely defined (e.g., the location and accessibility of reference areas, the availability of target species), specific work elements such as numbers of individuals to be collected, may have to be modified to meet the planned schedule. The schedule is also dependent on the seasonal flood duration of the Tombigbee River. It is estimated that the floodplain will be accessible throughout the sampling period.

Figure 6-1. Planned Schedule, Additional Ecological Studies of OU-2[1]

PLANNED SCHEDULE	SCHEDULE IN MONTHS								
TASK	May	June	July	Aug	Sept	Oct	Nov	Dec	Jan
1. Revised Work Plan Submittal	(May 16) ▼								
2. Selection of Reference Area	■								
3. Revised Work Plan Approval		(June 15) ▼							
4. Field Data Gathering		■	■	■					
5. Data Reduction and Evaluation			■	■	■	■			
6. Report Submission						(Oct. 28) ▼			

[1] *Schedule is contingent on EPA approval of work plan on specified date and timely approval of effects levels and exposure assumptions.*

FIGURE 6-1

7.0 REFERENCES

APHA. 1992. Standard Methods for the Examination of Water and Wastewater. American Public Health Association. Washington, D.C.

Branson, D.R., G.E. Blau, H.C. Alexander, and W.B. Neely. 1975. Bioconcentration of tetrachlorobiphenyl in rainbow trout as measured by an accelerated test. Trans. Am. Fish. Soc. 4:785-792.

DeGraaf, R.M., and D.D. Rudis. 1986. New England wildlife: Habitat, natural history, and distribution. U.S. Department of Agriculture, Forest Service, Northeastern Forest Experimental Station. General Technical Report NE-108, 491 p.

Foster, R.B. 1974. The potential use of the freshwater mussel as a monitor of copper. M.S. Thesis. Eastern Michigan University. 43p.

Foster, R.B. and J.M. Bates. 1978. Use of freshwater mussels to monitor point sources industrial discharges. Env. Sci. Tech. 12(8):958-962.

Green, R.H. and R.C. Young. 1993. Sampling to detect rare species. Ecological Applications 3(2):351-356.

Krzeminski, S.F., J.T., Gilbert, and J.A. Ritts. 1977. A pharmacokinetic model for predicting pesticide residues in fish. Arch. Environ. Contam. 5:157-165.

Lowery, G.H., Jr. 1974. The mammals of Louisiana and its adjacent waters. Louisiana State University Press, Baton Rouge, Louisiana. xxiii+565 p.

Newell, A.J., W.L. Griffis, C.M. Wise, E. Hopkins, and J.A. Barbita. 1987. Niagara River biota contamination project: Fish flesh criteria for piscivorous wildlife. New York State Department of Environmental Conservation, Technical Report 87-3, Division of Fish and Wildlife, Bureau of Environmental Protection. v+182 p.

Pentreath, R.J. 1973. The accumulation from water of Zn, Mn, Co, and Fe by the mussel, *Mytilus edulis*. J. Mar. Biol. Assoc. U.K. 53:127-143.

Thomann, R.V. 1981. Equilibrium model of fate of micropollutants in diverse aquatic food chains. Can. J. Fish. Aquat. Sci. 38:280-296.

U.S. Environmental Protection Agency (U. S. EPA). 1989. Risk assessment guidance for superfund volume II environmental evaluation manual, interim final. 1989. EPA/540/1-89/001. U. S. EPA Office of Emergency and Remedial Response, Washington, D.C.

Veith, G.D., D.L. DeFoe, and B.V. Bergstedt. 1979. Measuring and estimating the bioconcentration factor of chemicals in fish. J. Fish. Res. Can. 36:1040-1048.

Woodward-Clyde Consultants (WCC). 1993. Remedial investigation report. McIntosh Plant Site, Olin Corporation, McIntosh, Alabama. July.

Wilson, K.W. 1978. Transfer and transformation of pollutants by biological processes. Fifth FAO/SIDA Workshop, Via delle Terme di Caracalla, 00100 Rome, Italy.

APPENDIX A

APPENDIX A

PROTOCOLS

LIST OF PROTOCOLS

PROTOCOL 1

SAMPLING PROCEDURES FOR ABIOTIC MEDIA

1.0 SEDIMENT AND SOIL SAMPLING

Sediment and surface soil samples will be collected from the inundated water bodies (i.e., during the nonflood season) and the adjacent floodplain in OU-2 and the reference area.

Discrete surface sediment samples will be collected using stainless steel trowels/shovels in areas that are accessible to these hand sampling tools. In areas where there is significant water, such as the basin, the samples will be collected with an Ekman grab sampler. The Ekman sampler is designed to retrieve bulk sediments remotely from a 4- to 6-inch depth, which is the zone of biological activity in OU-2.

For discrete samples using the shovel/trowel (i.e., the soil samples from the floodplain areas), the sampling area will be first cleared of vegetation and/or debris. The sample will be collected to a depth of about 4 to 6 inches and then deposited in a stainless steel bowl. The sample will then be transferred to the appropriate container for analysis. The hole will be backfilled with native soils.

Sediments that are sampled using grab-type (e.g., Ekman dredge) samplers will be obtained by lowering the sampler to the sediment surface and releasing a weight down a messenger line to activate the closure mechanism, which excavates the surface sediments. Upon reaching the surface, the sample will be drained of free water and deposited in a stainless steel bowl set within a larger catch basin.

Soil and sediment samples will be mixed thoroughly to ensure that the sample is as representative as possible of the sample interval. Sample mixing will be done in round stainless steel bowls by stirring the material in circular fashion, occasionally turning the material over. After mixing, the sample will be placed in pre-labeled sample containers provided by the analytical laboratory. The sample containers then will be immediately

placed in coolers containing ice. The samples will be shipped from the site to the contract laboratory at approximately 4 ° C in these coolers. Sample designation, labeling and chain-of-custody are described in Section 3.0 of the Work Plan.

2.0 WATER SAMPLING (CLEAN HANDS-DIRTY HANDS TECHNIQUE)

Water samples will be collected from OU-2 and the reference area. Due to the low-level detection limits of the analytical methods to be used, the planned sample collection and handling techniques are designed to maintain a "cleanroom" environment around the samples at all times. This is particularly critical for the mercury analyses. A technique called "clean hands-dirty hands will be used (Fitzgerald and Watras 1989; Bloom 1994; Becker and others 1993). The clean hands dirty hands procedures described below are based on Bloom (1994) for mercury analyses. Similar procedures will be used for the samples for organic analyses since these samples will be collected concurrently.

Samples will be collected directly in the sample containers provided by the analytical laboratory. For the organic analyses (DDTr and HCB), sample containers will consist of 4-liter amber solvent-rinsed glass containers with Teflon®-lined screw tops. The mercury analyses containers will consist of either laboratory-cleaned 60 ml glass jars with Teflon®-lined screw tops or laboratory-cleaned 60 ml polyethylene jars.

Samples will be collected from a boat or by wading out to the sampling location. Care will be taken not disturb the sampling area prior to collection. A 'cleanroom' environment must be maintained around the samples at all times. The "clean hands-dirty hands" procedures process starts in the laboratory cleanroom, where the sample containers are cleaned and double bagged in polyethylene bags. Each sample container is thus contained in a "mini-cleanroom" during transport and storage. The sample bottles for mercury analyses will be shipped from the laboratory containing acidified ultra-clean water.

Sample collection will be done with a three-person field crew. All field crew members will wear tyvek that have been isolated from dust in plastic bags until use. Two pairs of gloves will be used by the sampling personnel designated to handle the sample jars,

an inner polyethylene glove and an outer vinyl glove. The outer glove will be clean room gloves that come in vacuum-sealed plastic bags. Once opened, the clean room gloves are potentially exposed to contamination and therefore only the wrist end on the bag should be opened. The unused gloves will be kept in the original bag and also inside a large Ziploc® bag. In the field, the double bagged sample container will be withdrawn from the box by the person designated "dirty hands." The outside bag is considered dirty, so "dirty hands" can pick it up, touch it, etc. To withdraw the bottle, "dirty hands" will open the outer bag, and hold it. Then, "clean hands" will reach into the bag carefully, open the inner bag avoiding touching inside the bag, and withdraw the bottle. "Clean hands" will then open the bottle with a plastic shrouded dedicated wrench. For the mercury containers, "clean hands" will pour the acidified ultra-clean water out of the bottle (away or downstream from the sampling point). (This is not necessary for the organic analysis samples because these sample containers will be shipped empty.) "Clean hands" will then rinse with sample water, and will collect the sample. Sampling in the rain will be avoided because rain has elevated concentration of mercury compared to most surface waters (Becker and others, 1993).

Once collected, the lid will be replaced tightly, and the bottle carefully replaced into the inner bag. "Clean hands" will reseal the inner bag, and "dirty hands" will reseal the outer bag. The additional crew member may perform as either a clean or dirty hands, depending upon what job is needed. The samples will be shipped to the laboratory in coolers containing ice. The samples for mercury analysis will be preserved with bromine monochloride within 24 hours of receipt by the laboratory. Sample designation, labeling, and chain-of-custody are described in Section 3.0 of the Work Plan.

3.0 DECONTAMINATION PROCEDURES

Prior to initiating the field work and between sample locations, the sampling equipment that is not dedicated and supplied by the laboratory will be decontaminated in the field. This will include the soil/sediment sampling tools, the Ekman dredge, the stainless steel bowls and mixing spoons.

All washwater that is collected during decontamination will be containerized for proper disposal/treatment by Olin. Specific decontamination procedures for sampling equipment is described below:

1. Clean with tap water and laboratory-grade, phosphate-free detergent, using a brush if necessary to remove particulate matter and surface films.

2. Rinse thoroughly with tap water.

3. Rinse thoroughly with deionized water.

4. Rinse twice with solvent (pesticide-grade isopropanol)

5. Rinse thoroughly with organic-free water and allow to air-dry as long as possible.

6. If organic-free water is not available, allow equipment to dry as long as possible. Do not rinse with deionized or distilled water.

7. Wrap with aluminum foil, if appropriate, to prevent contamination if equipment is to be stored or transported.

Solvents will not be used for cleaning of plastic items. Plastics may be used (instead of foil) to wrap equipment after cleaning if all traces of solvents have been removed. All decontamination fluids, except for tap water, must be applied using non-interfering containers and applicators. These should be made of glass, stainless steel or Teflon®. Pump sprayers, because of the presence of rubber and greased or oiled leather gaskets and seals, are generally acceptable only for applying tap water. The isopropanol will be applied with a Teflon® spray bottle.

To verify the adequacy of decontamination, rinsate samples from the sampling equipment will be obtained at a frequency of at least one per event (i.e., once during the water sampling and once during the soil/sediment sampling). The rinsate samples

will be analyzed for the same parameters as the media that were sampled with the equipment.

References

Fitzgerald, W.F. and C.J. Watras (1989) "Mercury in Superficial Waters of Rural Wisconsin Lakes," *Science of the Total Environmental*, 87/88: 223.

Bloom, Nicolas S. (1994, in press) "Mercury, a Case Study of Ultra-Clean Sample Handling and Storage in Aquatic Tracemetal Research," *Environmental Lab*.

Becker, S. D., Bingham, G.N., and Murphy, M. H. (1993) "Distribution of Mercury in a Lake Food Web," Poster presented at 14th Annual Meeting of the Society of Environmental Toxicology and Chemistry; Houston, Texas; November 14-18, 1993.

PROTOCOL 2

COPC ANALYTICAL METHODS

MERCURY ANALYSES IN SOIL/SEDIMENT AND BIOLOGICAL TISSUE (HAZLETON METHOD MP-HGE-MA)

DDTr AND HCB ANALYSES IN SOIL/SEDIMENT (HAZLETON METHOD MP-FWSS-MA)

DDTr AND HCB ANALYSES IN BIOLOGICAL TISSUE (HAZLETON METHOD MP-FWST-MA)

MERCURY ANALYSES IN WATER (FRONTIER GEOSCIENCES LOW DETECTION LIMIT METHOD)

MERCURY ANALYSES IN SOLIDS (FRONTIER GEOSCIENCES LOW DETECTION LIMIT METHOD)

DDTr AND HCB ANALYSES IN WATER AND SOIL/SEDIMENT (BATTELLE MODIFIED SW-846 LOW DETECTION LIMIT METHOD)

MERCURY ANALYSES IN SOIL/SEDIMENT AND BIOLOGICAL TISSUE (HAZLETON METHOD MP-HGE-MA)

Hazleton Environmental Services
QAU - DO NOT DUPLICATE

3 4 0189

MP-HGE-MA
PAGE: 1 OF 10
DATE: 01/17/92
REPLACES: Original
SECTION: 6005

ASSAY TITLE: Mercury

AREA OF APPLICABILITY: Hazleton Wisconsin, Inc.
Atomic Absorption

SCOPE:

This method is applicable to most materials including feeds, animal tissues, plants, soils, and food products.

PRINCIPLE:

Samples are digested with a mixture of sulfuric and nitric acids. Mercury is reduced with sodium borohydride for determination. The amount of mercury is determined at a wavelength of 253.7 nm by comparing the signal of the unknown sample (measured by the atomic absorption spectrophotometer with the MHS-20 hydride generation unit) with the signal of the standard solutions.

SENSITIVITY, PRECISION, AND ACCURACY:

The precision and accuracy of this assay have not been determined. Using a 2.0 g sample, the lowest detection limit of this assay is 0.025 ppm.

REFERENCE:

"Test Methods for Evaluating Solid Waste," EPA Publication No. SW-846, Second Edition, Methods 3030, 3040, or 3050; and 7470, U.S. EPA, Washington, D.C. (Revised April 1984).

Hazleton Environmental Services
QAU - DO NOT DUPLICATE

APPROVED BY: John C. Walton DATE: 1-10-92
John Walton
Staff Scientist/Section Leader
Inorganic Environmental Analysis

David C. Hills DATE: 1-14-92
David C. Hills
Manager
Inorganic Environmental Analysis

REVIEWED BY: Sherry R.W. Petsel DATE: 1-17-92
Sherry R.W. Petsel
Manager
Quality Assurance Unit

(1518D)

SAFETY PRECAUTIONS:

- Mercury and its salts are highly toxic. Use extreme care when handling mercury solutions and wash hands thoroughly afterward.
- When using sodium borohydride, sulfuric acid solutions, or sulfuric acid:nitric acid mixtures, avoid contact with skin and inhalation of vapors because these solutions and their vapors are corrosive. If any of these solutions come into contact with skin, immediately flush the skin with running water for at least 10 minutes.
- Handle potassium permanganate cautiously. Diluted solutions are mildly irritating and high concentrations are caustic.
- Observe all standard laboratory safety procedures as outlined in the Hazleton Wisconsin Safety Training Manual.

FUNDAMENTAL EQUATIONS:

$$Hg^{2+} + 2BH_4^- \text{ -----> } Hg + H_2 \uparrow + 3/2\ B_2H_6$$

INTERFERENCES:

No known interferences exist.

QUALITY ASSURANCE:

Strictly follow the following requirements to avoid possible contamination.

- Closely match the concentration of reagents in both samples and standards because acidity and viscosity affect instrument sensitivity.
- Include a reagent blank with every run. Take it from the first step of sample preparation through the actual analysis.
- Include a duplicate sample with every run (ideally at a frequency of approximately 5% to 10%) and take it from the first step of sample preparation through the actual analysis.
- Include a recovery as appropriate and take it from the first step of sample preparation through the actual analysis.

- Include a digestion control or a validated control sample (if available) as appropriate and take it from the first step of sample preparation through the actual analysis.
- Use deionized water and acid-washed glassware.
- Ensure that the sample is completely digested. Contact the area supervisor with any problems.
- Refer to the Standard Operating Procedures (SOPs) for Inorganic Analysis.
- See the Instrument Operating Procedure (IOP) for the appropriate atomic absorption spectrophotometer and hydride generation unit.
- Clean and rinse all tubing and cells before a day's run by running deionized water and then methanol through all components and drying them with a flow of nitrogen.
- Test the sulfuric acid and potassium permanganate solutions for possible mercury contamination before use.
- Consider a blank greater than the lowest standard to be significant and take it into consideration according to the SOPs for Inorganic Analysis.

APPARATUS:

- Round-bottomed flasks, 300 mL with two short necks, carrying 35/25 center and 18/9 side-ground glass joints
- Water condensers, 2.5 cm in diameter, 30 cm long, 35/25 ground glass balloon bottom
- Heating mantles, 335 watts, 300 mL, with a continuous heat variance
- Volumetric flasks, Class A, acid-washed
- Pipettes, Class A
- Mercury hollow cathode lamp or electrodeless discharge lamp
- Analytical balance, ±0.01 g for samples, ±0.0001 g for standards and reagents
- Magnetic stir plate
- Variac to control digestion temperature
- Glass stopper with 18/9 ground glass fitting

- Rack for holding digestion apparatus, including clamps for condensers, rack for mantles, and electrical socket apparatus (four female sockets with one male plug) for heating mantles
- Cold water source and tubing to run condenser system
- Boiling chips, acid-washed, 50 mL
- Erlenmeyer flasks for storing reagents
- Graduated cylinder, acid-washed
- Atomic absorption spectrophotometer
- Hydride generation unit, including appropriate quartz cell for vapor analysis and appropriate tubing

Note: Equivalent equipment may be substituted.

REAGENTS:

- 1,000 ppm mercury stock solution, Fisher certified or equivalent.

- Mercury working standard: Recommended concentration is 1 ppm in 20% H_2SO_4. Prepare every 3 months.

  - Serial dilute stock solution by factors of 10 to 1 ppm in 100 mL in 20% H_2SO_4.

- Mercury working standards: Recommended concentrations are 0.01 and 0.001 ppm in 20% sulfuric acid, preserved with one drop of potassium permanganate solution. Prepare both on each day of use by serial dilutions of the 1 ppm working standard.

- 3% sodium borohydride in 1% sodium hydroxide: Dissolve 3.0 g sodium borohydride and 1.0 g sodium hydroxide in 100 mL deionized water. When in solution, vacuum filter the mixture using a 0.45-micron filter disc. Prepare fresh solution each day of use to avoid decomposition and liberation of hydrogen.

- Potassium permanganate saturated solution: Weigh 8.0 g of potassium permanganate into a 200-mL volumetric flask, add deionized water to dissolve it, fill the flask to volume, and mix the solution by inversion.

- Concentrated nitric acid, AR grade (marked and kept separate for mercury determination only).

- Concentrated sulfuric acid, AR grade (marked and kept separate for mercury determination only).
- 20% sulfuric acid (v/v): Place 2,400 mL deionized water into a large (4-L) Erlenmeyer flask. Carefully add 600 mL of concentrated sulfuric acid, swirl to mix the solution, and allow it to cool.
- Sulfuric acid:nitric acid mixture (4:1): Mix 4 parts concentrated sulfuric acid with 1 part nitric acid. Carefully swirl to mix the solution.
- 20% hydroxylamine hydrochloride solution: Dissolve 40.0 g in 160 mL deionized water.

Note: Equivalent reagents may be substituted.

PROCEDURE:

1. Weigh a 2- to 4-g sample into an acid-washed, 300-mL round-bottomed flask.

   1.1 Add boiling chips and turn on the cold water for the condenser system.

   1.2 Ensure that the outlet is in the drain and that the pressure is low enough to maintain the system without leakage.

2. Carefully add 25 mL of the sulfuric acid:nitric acid mixture to each of the flasks.

   2.1 Place the flasks in a heating mantle and insert the condensers.

   2.2 Add a stopper to the side arm.

3. Begin heating. If necessary, add very small amounts of nitric acid through the side arm to prevent charring. For example, if the sample begins to darken and there are no brown fumes, add nitric acid. Foaming may occur just before charring. Fats and oils are likely to char.

4. Allow the samples to reflux for 1 hour.

5. Turn off the heat.

6. After cooling the condensers and flasks for about 15 minutes, lightly rinse them with deionized water. Allow them to cool for a few more minutes.

7. Disconnect the condensers and remove the flasks from the heating mantles.

   Note: If desired, start a second batch and monitor it during Steps 8 through 10 of the first batch. Observe Steps 1 through 3 constantly.

8. Add a small amount of saturated potassium permanganate solution to each digested sample and swirl it. Repeat this step until a dark color persists.

9. Quantitatively transfer the digest to an acid-washed, 100-mL volumetric flask. Use deionized water for rinsing.

10. Add 20% hydroxylamine hydrochloride in drops while swirling the solution until the permanganate color disappears. The solution usually becomes colorless, but some other color may remain depending on the nature of the particular sample.

    10.1 Fill the flask to volume with deionized water and mix the solution by inversion.

11. Proceed to the Determination section.

12. After all digestions are complete, turn off the water to the condenser system.

Determination

1. Determine the signal of the standards and samples with an atomic absorption spectrophotometer and a hydride generation unit according to the appropriate IOP.

2. For the instrument variables (wavelength, slit setting, etc.), refer to the "Standard Conditions for Mercury" in the appropriate atomic absorption methods manual.

   2.1 Install the lamp and allow it to warm up. Turn on the recorder and align the cell.

   2.2 Set the operating mode on the spectrophotometer for use with the appropriate (MHS-20) hydride generation unit.

   2.3 Turn on the gas supply (argon).

   2.4 Turn on the power of the MHS-20 controller. Select the $NaBH_4$ mode and adjust the temperature of the cell to 200°C.

   Note: Never use the instrument in the $SnCl_2$ mode when using sodium borohydride.

   2.5 Fill the reservoir with sodium borohydride solution.

3. Purge the system.

   3.1 After the temperature light turns on, set PURGE I to 40 seconds, REACTION to 0 seconds, and PURGE II to 0 seconds.

      3.1.1 Put the empty reaction flask on assembly and push START.

      3.1.2 Wait until the start indicator light turns off, then zero the display.

      3.1.3 Repeat Step 3.1 if necessary.

   3.2 Remove the reaction flask and set PURGE I, REACTION, and PURGE II according to the appropriate hydride generation manual.

4. Read each of the samples and standards using the following techniques.

   4.1 Dispense 10 mL of 20% sulfuric acid solution into the reaction flask and add one drop of the potassium permanganate solution.

      4.1.1 Put the flask on the hydride generation assembly and push START.

4.1.2 When the start indicator light turns off, remove and empty the reaction flask.

4.1.3 Rinse the flask completely with deionized water.

4.2 Repeat Step 4.1 for all standards and samples. Measure the sample size and dilute the total volume of the reaction to 10.0 mL with 20% sulfuric acid.

4.2.1 Record the aliquot and sample number on the chart.

4.2.2 After analyzing samples with an extremely high mercury content, check for contamination of the system and reaction flask by running a reagent blank.

4.3 Read the standards before and after the group of samples. Use a range of 0.002 to 0.05 µg for each treatment, including 0.002, 0.005, 0.01, 0.02, 0.03, and 0.05 µg.

4.4 Usually read samples using a 10-mL reaction.

4.4.1 If this is too high, take smaller reactions.

4.4.2 If necessary, dilute the sample by diluting an aliquot to volume with 20% sulfuric acid. Then read an appropriate reaction volume from the dilution.

CALCULATIONS:

Perform calculations by preparing a plot of concentration (x-axis) in µg/mL versus signal or absorbance (y-axis). Under the Beer-Lambert Law, the graph is linear (or nearly so), and the concentration of the unknown samples is determined by interpolation.

For computer calculations, enter the raw data (peak heights) and perform calculations by a least squares regression plot of peak height versus concentration.

Formula

$$S = \frac{C \times V \times D}{W \times R}$$

Where:

S = calculated concentration in ppm or µg/L
C = concentration from curve or computer projection in µg
V = volume of sample
W = sample size in g or mL
D = dilution factor
R = reaction volume

Report results using the mnemonic HGE.

DDTr AND HCB ANALYSES IN SOIL/SEDIMENT (HAZLETON METHOD MP-FWSS-MA)

Hazleton Environmental Services
QAU - DO NOT DUPLICATE

3 4 0195

MP-FWSS-MA
PAGE: 1 OF 14
DATE: 7/23/93
REPLACES: 8/26/92
SECTION: 6004

ASSAY TITLE: Determination of Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) in Soils and Sediments

AREA OF APPLICABILITY: HES, Inc.
Pesticide Residue

SCOPE:

This method covers the determination of organochlorine pesticides and PCBs in soil and sediment samples using gas chromatography with electron capture detection (GC-EC). It is to be used in conjunction with the analysis of all soil and sediment samples received under contract with the United States Department of the Interior Fish and Wildlife Service (USDI-FWS). The following pesticides and PCB Aroclor mixtures are calibrated and analyzed for under this method:

4,4'-DDE	Hexachlorobenzene (HCB)	Oxychlordane	Toxaphene
4,4'-DDD	Beta BHC	Alpha chlordane	PCB-1242
4,4'-DDT	Alpha BHC	Gamma chlordane	PCB-1248
O,P'-DDE	Gamma BHC (Lindane)	Trans nonachlor	PCB-1254
O,P'-DDD	Dieldrin	Endrin	PCB-1260
O,P'-DDT	Heptachlor epoxide	Mirex	Total PCB

PRINCIPLE:

Soil and sediment samples are mixed with anhydrous sodium sulfate and soxhlet extracted with methylene chloride. The resulting extract is filtered, concentrated, and exchanged to hexane. Contaminants may be removed from the extracts using gel permeation chromatography, column chromatography, with florisil and silica gel separation, and mercury cleanup for the elimination of sulfur. Quantitative determination is done using gas-liquid chromatography and GC-ECD. Results are reported in milligrams per kilogram (mg/kg) on a dry-weight basis.

SENSITIVITY:

The method detection limits presented in Attachment 1 represent the sensitivities that can be achieved in a soil matrix in the absence of interferences.

PRECISION AND ACCURACY:

The precision and accuracy of this method are presented in Attachment 2.

REFERENCES:

1. U.S. Environmental Protection Agency (EPA), Method 608 Federal Register, 49(209):43321-43336, (October 16, 1984).

2. "Test Methods for Evaluating Solid Waste," SW-846, Method 8080 (September 1986).

3. "Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11," 40 CFR 136, Appendix B (October 26, 1984).

APPROVED BY: Tod Noltemeyer DATE: 7/21/93
Tod Noltemeyer
Supervisor
Pesticide Residue

APPROVED BY: David C. Hills DATE: 7-16-93
David C. Hills
V.P. Laboratory Operations

REVIEWED BY: Amy L Austin DATE: 7/16/93
Amy L. Austin
Supervisor
Quality Assurance Unit

SAFETY PRECAUTIONS:

- The toxicity or carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each analyst is responsible for maintaining awareness of OSHA regulations regarding safe handling of the chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst.

- The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: P,P'-DDT, P,P'-DDD, the BHCs and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA-approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

- Observe all standard laboratory safety procedures as outlined in the HES, Inc. Safety Training Manual.

INTERFERENCES:

- Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample-processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

- Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending on the nature and diversity of the site being sampled. Cleanup procedures such as gel permeation chromatography (GPC), Florisil cleanup, and sulfur removal (using elemental mercury) are available for the most common interferences encountered.

QUALITY ASSURANCE:

Samples are prepared and analyzed in sets of 20 samples or less. Each sample set, at a minimum, must contain a method blank and a laboratory control spike. A matrix duplicate and matrix spike must also be prepared and analyzed with every set of 20 samples when sufficient sample quantity exists.

- Method Blank: A method blank is extracted and analyzed with every set of 20 samples or whenever samples are extracted, whichever is more frequent.

- Control Spike: A laboratory control spike is extracted and analyzed with every set of 20 samples or less. The control spike is prepared by spiking blank sand with a representative list of target analytes at approximately 10 to 50 times the contract required detection limit. Average recoveries of the spiked compounds should be within 80% to 120%.

- Sample Duplicate: A sample duplicate should be extracted and analyzed with every set of 20 samples processed when sufficient sample quantity exists.

- Matrix Spike: A matrix spike should be extracted and analyzed with every set of 20 samples processed when sufficient sample quantity exists. The matrix spike is prepared by adding target analytes at 10 to 50 times the contract required detection limit.

  Recoveries of the control spikes and matrix spikes are calculated using the following equation:

  $$\text{Control/Matrix spike percent recovery} = \frac{SSR - SR}{SA} \times 100\%$$

  Where: SSR = Spiked sample results
  SR = Sample results
  SA = Spike added from spiking mix

  The relative percent difference (RPD) between duplicate values for each component found in the sample is to be calculated using the following equation:

  $$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100\%$$

  Where: D_1 = First sample value
  D_2 = Second sample value (duplicate)

APPARATUS:

- Soxhlet extraction apparatus including condensers and heating mantles.
- Beaker, 250-500 mL, Pyrex® glass.
- Kuderna-Danish (K-D) apparatus, consisting of 10-mL graduated (1-mL graduations) concentrator tubes, 500-mL evaporative flask, and three - ball macro snyder columns.
- Pyrex glass wool. Pre-rinse glass wool with appropriate solvents to ensure its cleanliness.
- Teflon® boiling chips, approximately 10/40 mesh.

- Powder funnels, 65 mm x 108 mm, with Whatman No. 4 filters.
- Balance, analytical, capable of accurately weighing ±0.0001 g.
- Water bath, heated, with concentric ring cover, capable of temperature control within ±2°, to be used in a hood.
- Muffle furnace, capable of operating at a temperature up to 400°C.
- N-Evap nitrogen evaporation device, Organomation Associates, Inc.
- Gas chromatograph, analytical system complete with gas chromatograph and all required accessories including syringes, analytical columns, gases, electron capture detector, and strip-chart recorder with recording integrator. A data system is required for measuring peak areas or peak heights and recording retention times.

Note: Equivalent equipment may be substituted.

REAGENTS:

- Acetone, hexane, iso-octane, methanol, methylene chloride, petroleum ether, acetonitrile (all pesticide quality or equivalent)
- Sodium sulfate (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.
- Mercury

STANDARD PREPARATION

1. Pesticide Matrix Spiking Solutions

The pesticide matrix spiking solutions should contain the following compounds at a concentration of 20 µg/mL in methanol, acetone or iso-octane.

Hexachlorobenzene	Dieldrin
Alpha-BHC	P,P'-DDE
Gamma-BHC	P,P'-DDD
Oxychlordane	Endrin
Heptachlor epoxide	O,P'-DDT
Alpha-chlordane	O,P'-DDD
Trans-nonachlor	O,P'-DDT
Gamma-chlordane	Mirex
P,P'-DDE	2,4,5,6-Tetrachloro-m-xylene

Surrogate Spiking Solution

Prepare a 100 µg/mL solution of 2,4,5,6-tetrachloro-m-xylene (TMX) in methanol or acetone.

Instrument Calibration Standards

1. Column Evaluation Standard - Prepare a mixed standard containing 0.1 µg/mL of 4,4'-DDT and endrin in hexane.

2. Individual Standard Mixtures - These include all single-component organochlorine pesticides. Prepare two mixtures of the individual component standards to maximize resolution of those compounds on both columns to be used in the analysis. Prepare the two individual standard mixtures in hexane or iso-octane at the concentrations specified:

STANDARD MIX - 1

Pesticide	Conc A	Conc B	Conc C
Hexachlorobenzene	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Gamma-BHC	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Oxychlordane	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Alpha-chlordane	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Gamma-chlordane	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
4,4'-DDE	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
4,4'-DDD	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
4,4'-DDT	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Endrin	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Tetrachloro-m-xylene	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL

STANDARD MIX - 2

Pesticide	Conc A	Conc B	Conc C
Alpha-BHC	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Heptachlor epoxide	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Trans-nonachlor	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
O,P'-DDE	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
O,P'-DDD	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
O,P'-DDT	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Dieldrin	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Mirex	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Tetrachloro-m-xylene	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL

3. Multi-response Pesticide Standards and Beta-BHC - Prepare the multi-response pesticides in a single mixture containing the following compounds and concentrations in hexane or iso-octane:

Pesticide	Conc A	Conc B	Conc C
Beta BHC	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Toxaphene	0.2 µg/mL	1.0 µg/mL	10.0 µg/mL

4. PCB Stock Standards - Prepare stock solution of Aroclors 1242, 1248, 1254, and 1260 at concentrations of 20 µg/mL in hexane.

5. PCB Working Standards - Use the following concentrations for the working standards for the individual PCB Aroclors (note that all Aroclors must be prepared as separate standard solutions):

Conc A	Conc B	Conc C
0.2 µg/mL	1.0 µg/mL	10 µg/mL

PROCEDURE:

1. Decant any standing water from the samples.

2. Homogenize the samples by shaking the sample container or by stirring the contents of the sample container with a spatula. If this is not possible because there is too much sample in the container or the consistency of the sample does not permit stirring, the sample may be placed into another container or spread out in an aluminum pan for mixing.

Sample Extraction

1. Blend 10 g of soil or sediment with 40 g of anhydrous sodium sulfate in a 250-mL beaker. If 10 g of sample is not available, then remove at least 1 g for percent moistures and weigh the remainder for extracting. For wet samples, more sodium sulfate may be required. If a sufficient amount has been added, the sample will appear granular.

2. Add 100 µL of the pesticide spiking solutions to the matrix spike and the control spike.

3. Add 20 µL of the TMX surrogate spiking solution to all samples and the method blank.

4. Allow the soil/sediment and sodium sulfate to dry under a hood for a couple of hours, stirring it occasionally.

5. Place 1 to 5 g of sample onto a preweighed aluminum pan. Dry the sample at least 16 hours in an oven at 105°C. Weigh the pan and sample again after drying. Calculate the percent moisture as follows:

$$\% \text{ Moisture} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Wet weight}} \times 100\%$$

6. Load the prepared sample into the Soxhlet extractor between two plugs of preextracted glass wool.

   6.1 Place 250 mL of methylene chloride into a prerinsed 500 mL Erlenmeyer flask containing three to five Teflon boiling chips.

   6.2 Attach the flask to the extractor.

   6.3 Add 100 mL of methylene chloride to the mixing beaker, swirl, and add the solvent to the extractor prior to attaching the condenser.

   6.4 Adjust the temperature of the heating mantle so that the extractors cycle at a rate of 12 to 15 cycles per hour. Allow the system to cycle for 16 to 20 hours.

7. Allow the extract to cool after the extraction is complete. Rinse the condenser with extraction solvent and drain the Soxhlet apparatus into the bottom collection flask.

8. Pour the extract through a Whatman No. 4 filter into a 500-mL K-D flask fitted with a 10 mL concentrator tube. Attach a three-ball snyder column to the K-D flask and concentrate the extract on a hot water bath, adjusting the temperature so that the concentration is completed within 15 to 20 minutes.

9. When the apparent volume reaches approximately 5.0 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Bring up to a volume of 10 mL with methylene chloride.

Extract Cleanup

1. Proceed with the appropriate cleanups as necessary (GPC; OP-6004-LP.001, silica gel separation; OP-6004-TLP.003, mercury shakeout to remove sulfur; OP-6004-DLP.004). All soil samples should be cleaned using GPC.

2. Take extract to a final volume of 2 mL in hexane.

Instrumental Analysis

1. Recommended GC Columns and GC Operating conditions

1.1	Column 1:	30 m x 0.53-mm i.d., DB-608 Megabore
	Inst conditions:	INJ temperature 200°C, DET temperature 300°C
	Temperature program:	180°C to 220°C at a rate of 1°C/minute, 220°C to 270°C at a rate of 5°C/minute, hold for 5 minutes
	Carrier gas:	Helium at 6.5 mL/minute
	Makeup gas:	Nitrogen at 30 mL/minute
1.2	Column 2:	30 m x 0.53-mm i.d., DB-1701 Megabore
	Inst conditions:	INJ temperature 200°C, DET temperature 300°C
	Temperature program:	180°C to 220°C at a rate of 1°C/minute, 220°C to 270°C at a rate of 5°C/minute, hold for 5 minutes
	Carrier gas:	Helium at 6.5 mL/minute
	Makeup gas:	Nitrogen at 30 mL/minute
1.3	Column 3:	30 m x 0.53-mm i.d., DB-5 Megabore
	Inst conditions:	INJ temperature 200°C, DET temperature 300°C
	Temperature program:	180°C to 220°C at a rate of 1°C/minute, 220°C to 270°C at a rate of 5°C/minute, hold for 5 minutes
	Carrier gas:	Helium at 6.5 mL/minute
	Makeup gas:	Nitrogen at 30 mL/minute

2. Instrumental Analysis

All extracts are analyzed using GC-EC. The sample extracts are analyzed and compared with external standards for qualitative and quantitative purposes. If the extract has been separated into a pesticide and a PCB fraction using silica gel, then each fraction is analyzed only for those analytes expected in the fraction.

3. Pesticide Analysis

3.1 The pesticides are analyzed on a gas chromatograph with wide-bore capillary columns and an electron capture detector. An initial injection of an evaluation mixture containing 4,4'-DDT and endrin is made. Breakdown of the 4,4'-DDT into 4,4'-DDD and 4,4'-DDE and/or endrin into endrin ketone and endrin aldehyde must not exceed 20%. The percent breakdown is calculated using Equation 1.0. If the breakdown for either 4,4-DDT or endrin does exceed 20%, the run cannot be used for analysis of samples.

Equation 1.0:

$$\%\text{DDT Breakdown} = \frac{\text{Area of 4,4'-DDD} + \text{4,4'-DDE}}{\text{Area of 4,4'-DDT} + \text{4,4'-DDD} + \text{4,4'-DDE}} \times 100\%$$

$$\%\text{Endrin Breakdown} = \frac{\text{Area of endrin aldehyde + endrin ketone}}{\text{Area of endrin + endrin aldehyde + endrin ketone}} \times 100\%$$

3.2 A three-point calibration of the Aroclors and the pesticide Standard Mixes A, B and C are analyzed prior to sample analysis. The correlation coefficient of the linear regression of the three-point standards and zero must be greater than 0.995 for each analyte in order to be able to quantitate.

3.3 Five samples may be analyzed followed by another injection of the evaluation mixture. The evaluation mixture must continue to exhibit less than 20% breakdown of 4,4'-DDT and endrin.

3.4 Five more samples may be analyzed followed by an injection of one of the B pesticide standards and either the beta-BHC/toxaphene or one of the Aroclor B standards. The peak areas of the analytes in each ongoing B standard must be within 20% of the peak areas of the same initial standard. The sequence of samples, the evaluation mixture, and the B standards may continue as long as the acceptance criteria are met. The last sample injection must be followed by an injection of all B pesticide standard mixes.

3.5 If any standard does not meet the acceptance criteria, then that standard and any samples analyzed after it, may be reinjected. If the standard is still unacceptable, the analytical run is completed with that standard and a new initial calibration must be run in order to analyze more samples.

Analytical Sequence

1	Evaluation Mixture
2	Aroclor 1242-A
3	Aroclor 1242-B
4	Aroclor 1242-C
5	Aroclor 1248-A
6	Aroclor 1248-B
7	Aroclor 1248-C
8	Aroclor 1254-A
9	Aroclor 1254-B
10	Aroclor 1254-C
11	Aroclor 1260-A
12	Aroclor 1260-B
13	Aroclor 1260-C
14	Beta BHC/Toxaphene A
15	Beta BHC/Toxaphene B
16	Beta BHC/Toxaphene C
17	Standard Mix 1-A
18	Standard Mix 1-B
19	Standard Mix 1-C
20	Standard Mix 2-A
21	Standard Mix 2-B
22	Standard Mix 2-C
23 - 27	Five samples
28	Evaluation Mixture
29 - 33	Five samples
34	Standard Mix 1-B or 2-B
35	Beta-BHC/Toxaphene-B or one of the Aroclor-B
36	Repeat Steps 23 through 35 ending the sequence with the three B pesticide standards.

3.6 Retention time windows (RTWs) of each analyte are established as follows.

3.6.1 Analytes eluting prior to 14 minutes have an RTW of ±0.07 minutes of the initial B standard retention time. For example, a peak with an initial retention time of 10 minutes has a RTW of 9.93 to 10.07 minutes. The RTW for any analytes eluting later than 14 minutes, but prior to 20 minutes, will be 0.6% of the initial B standard retention time. For example, a peak with an initial retention time of 17 minutes has a window of 16.90 to 17.10 minutes. The RTW for analytes eluting 20 minutes or later will be established as ±0.5% of the initial B standard retention time. The retention times for the ongoing standards must fall within their respective RTW in order to continue sample analysis. The sample peaks being analyzed must be within the calibration range of the initial standards. A peak is qualitatively identified if the retention time falls within the RTW established for an analyte of interest.

3.7 The tentatively identified sample peak is quantified using Equation 1.1.

Equation 1.1

$$Soil: \frac{(A1)\ (C)\ (V)\ (D)}{(A2)\ (M)} = ug/kg$$

Where:
A1 = Area of sample peak
A2 = Area of Midpoint Standard peak
C = Concentration of Midpoint Standard (µg/mL)
V = Extract volume (mL)
D = Dilution factor
M = Mass of sample extracted (kg)

3.8 Confirmation (second column)

3.8.1 Second-column confirmation is qualitative only; therefore only the injection of a midpoint standard is required; however the evaluation mixture containing DDT and Endrin must also be injected and demonstrate that the column breakdown of those two compounds does not exceed 20%.

3.8.2 The peak of interest must fall within the RTW on the second column to be confirmed. However, the analyst's judgment may also be used in deciding if a peak does or does not confirm.

3.8.3 The confirmation run may be used to quantitate compounds found in the sample if coeluting peaks encountered in the primary quantitative run interfere with accurate quantification. If the confirmation run is used as a "secondary quantitation run" for selected compound, this use must be noted and those compounds qualitated on the run documented. In those cases where quantitation is performed, all relevant calibration criteria will apply for those compounds to be quantified including: initial calibration, continuing calibration, and DDT/Endrin breakdown.

4. PCB Analysis

4.1 The individual PCBs are identified by pattern recognition. Individual PCB quantification is done by summing the areas of at least five sample peaks and also summing the same five peaks in the initial standard closest in area to the sample (for example, the A standard of Aroclor 1242, if the amount of Aroclor 1242 in the sample is near the detection limit). These area sums are used in Equation 1.1 to calculate the concentration of PCBs present in the sample.

4.2 Total PCB's are obtained by summing the individual Aroclors quantified.

Mass Spectrometry Confirmation

1. Ten percent of the samples and at least one sample per matrix must be analyzed by gas chromatography/mass spectroscopy (GC/MS) if any of the samples in a set confirm for any analyte that has a concentration in the extract greater than 10 ng/μL. The blank associated with any samples requiring GC/MS confirmation must also be analyzed. At least one standard of any analyte being confirmed must be injected prior to and after analysis of the samples. The results presented on the Sample Result Form must state if the GC/MS confirmation was required for the sample and if the analytes of interest confirmed.

2. If an analyte appears to be present, based on electron capture gas chromatography, at a concentration higher than the limit of detection for mass spectrometry, and the identity of that compound can not be confirmed or tentatively confirmed by mass spectrometry, it should be assumed that the electron capture result is due to an interference. The report should be adjusted (for all samples controlled by the mass spec sample in question) to read < the former result. The detection limit is redefined as the apparent concentration due to the interference.

Documentation and Reporting

Follow all general standard operating procedures for the complete documentation of all standard and sample preparation as well as instrumental analysis and analyte calculations. Raw data and hardcopies of the results must be filed. A cover letter, a diskette summary of the results, and a Matrix Spike Recovery and Duplicate Analysis Form will be sent to the client.

Hazleton Environmental Services

QAU - DO NOT DUPLICATE

3 4 0202

MP-FWSS-MA
ATTACHMENT 1

METHOD DETECTION LIMITS (MDL)

Compound	MDL (µg/kg)	Std Reporting Detection Limit (µg/kg)
P,P'-DDE	1.1	10
P,P'-DDD	1.1	10
P,P'-DDT	1.4	10
O,P'-DDE	1.0	10
O,P'-DDD	1.3	10
O,P'-DDT	0.8	10
Hexachlorobenzene (HCB)	1.6	10
Alpha BHC	1.5	10
Gamma BHC	1.6	10
Dieldrin	1.0	10
Heptachlor epoxide	1.0	10
Oxychlordane	1.0	10
Alpha chlordane	1.0	10
Gamma chlordane	1.1	10
Trans-nonachlor	1.1	10
Endrin	1.0	10
Mirex	0.8	10
Toxaphene	10.5	50
PCB-1242	19.9	50
PCB-1248	17.9	50
PCB-1254	10.1	50
PCB-1260	29.0	50

Note: Validated MDLs determined according to the protocol outlined in 40 CFR 136, Appendix B, October 26, 1984, "Definition and Procedure for the Determination of the Method Detection Limit."

Hazleton Environmental Services

QAU - DO NOT DUPLICATE

MP-FWSS-MA
ATTACHMENT 2

METHOD PERFORMANCE
Organochlorine Pesticides/PCBs
Soil Matrix

Compound	CAS No.	MDL µg/kg	Average % Recovery	% Relative Deviation	Windows
P,P'-DDE	72-55-9	1.1	85	9.3	66-103
P,P'-DDD	72-54-8	1.1	74	27	21-127
P,P'-DDT	50-29-3	1.4	77	9.5	59- 96
O,P'-DDE	3424-82-6	1.0	98	4.4	83-100
O,P'-DDD	53-19-0	1.3	84	9.6	65-103
O,P'-DDT	789-02-6	0.8	96	11	74-119
HCB	118-74-1	1.6	84	11	66-105
Alpha BHC	319-84-6	1.5	78	16	46-110
Gamma BHC	58-89-9	1.6	78	12	53-102
Dieldrin	60-57-1	1.0	96	14	67-124
Heptachlor epoxide	1024-57-3	1.0	97	18	62-132
Oxychlordane	27304-13-8	1.0	96	18	60-130
pha chlordane	5103-71-9	1.0	80	8.7	62- 97
Gamma chlordane	5103-74-2	1.1	84	11	62-105
Trans-nonachlor	39765-80-5	1.1	92	6.9	78-105
Endrin	72-20-8	1.0	91	12	67-115
Mirex	2385-85-5	0.8	104	15	74-135
Toxaphene*	8001-35-2	10.5	97	9.6	77-116
PCB-1242	53469-21-9	19.9	86	24	37-134
PCB-1248	12672-29-6	17.9	86	12	62-110
PCB-1254	11097-69-1	10.1	91	14	63-119
PCB-1260*	11096-82-5	29.0	96	9.2	78-114

Note: Routinely prepared matrix and control spikes do not include all analytes listed in the above tables. Those compounds footnoted with an "*" represent method performance results generated from clean soil spikes and a limited number of data points and may not be representative of the true method performance that may routinely be achieved in actual field samples.

DDTr AND HCB ANALYSES IN BIOLOGICAL TISSUE (HAZLETON METHOD MP-FWST-MA)

Hazleton Environmental Services
QAU - DO NOT DUPLICATE

3 4 0204

MP-FWST-MA
PAGE: 1 OF 15
DATE: 07/01/93
REPLACES: 08/26/92
SECTION: 6004

PROCEDURE TITLE: Determination of Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) in Biological Tissues

AREA OF APPLICABILITY: HES, Inc.
Pesticide Residue

SCOPE:

This method covers the determination of organochlorine pesticides and PCBs in biological tissues using gas chromatography with electron capture (GC-EC) detection. This method is to be used in conjunction with the analysis of all tissue samples received under contract with the United States Department of the Interior Fish and Wildlife Service (USDI-FWS). The following pesticides and PCB Aroclor mixtures are calibrated and analyzed for under this method:

4,4'-DDE	Hexachlorobenzene (HCB)	Oxychlordane	Toxaphene
4,4'-DDD	beta-BHC	alpha-Chlordane	PCB-1242
4,4'-DDT	alpha-BHC	gamma-Chlordane	PCB-1248
O,P'-DDE	gamma-BHC (Lindane)	trans-Nonachlor	PCB-1254
O,P'-DDD	Dieldrin	Endrin	PCB-1260
O,P'-DDT	Heptachlor epoxide	Mirex	Total PCB

PRINCIPLE:

Biological matrices, previously ground and homogenized, are mixed with anhydrous sodium sulfate and extracted with methylene chloride using Soxhlet extraction. The resulting extract is then concentrated and subsequently cleaned up using gel permeation chromatography (GPC). Optional cleanups such as column chromatography silica gel partitioning, and mercury cleanup for the removal of sulfur may be used to provide further extract cleanup as necessary. Quantitative determination is effected via gas-liquid chromatography (GLC) employing electron capture detection. Results are reported in milligrams per kilogram (mg/kg).

SENSITIVITY, PRECISION, ACCURACY:

The method detection limits in Attachment 1 represent the sensitivities that can be achieved in a biological matrix in the absence of interferences.

The precision and accuracy of this method are presented in Attachment 2.

REFERENCES:

United States Environmental Protection Agency (EPA) Method 608, Federal Register, 49, (209): 43321-43336, (October 16, 1984).

Test Methods for Evaluating Solid Waste, SW-846, Method 8080, (September 1986).

Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11, 40 CFR 136, Appendix B, (October 26, 1984).

APPROVED BY: Tod Noltemeyer DATE: 6/29/93
Tod Noltemeyer
Supervisor
Pesticide Residue

APPROVED BY: David C. Hills DATE: 6-29-93
David C. Hills
V.P. Laboratory Operations

REVIEWED BY: Amy L. Austin DATE: 6/29/93
Amy L. Austin
Supervisor
Quality Assurance Unit

SAFETY PRECAUTIONS:

The toxicity or carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each analyst is responsible for maintaining awareness of OSHA regulations, the HES, Inc. Safety Training Manual, and material safety data sheets, regarding safe handling of chemicals used in this method.

The following analytes have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

INTERFERENCES:

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample-processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending on the nature and diversity of the site being sampled. Cleanup procedures such as GPC, Florisil cleanup, and sulfur removal (using elemental mercury) are available for the most common interferences encountered.

QUALITY ASSURANCE:

Samples are prepared and analyzed in sets of 20 samples or less. Each sample set, at a minimum, must contain a method blank and a laboratory control spike. A matrix duplicate and matrix spike must also be prepared and analyzed with every set of 20 samples when sufficient sample quantity exists.

- Method Blank: A method blank is extracted and analyzed with every set of 20 samples or whenever samples are extracted, whichever is more frequent.

- Control Spike: A laboratory control spike is extracted and analyzed with every set of 20 samples or less. The control spike is prepared by spiking tuna fish with a representative list of target analytes at approximately 10 to 50 times the contract required detection limit. Average recoveries of the spiked compounds should be within 80% to 120%.

- Sample Duplicate: A sample duplicate should be extracted and analyzed with every set of 20 samples processed when sufficient sample quantity exists.

- Matrix Spike: A matrix spike should be extracted and analyzed with every set of 20 samples processed when sufficient sample quantity exists. The matrix spike is prepared by adding target analytes at 10 to 50 times the contract required detection limit.

Recoveries of the control spikes and matrix spikes are calculated using the following equation:

$$\text{Control/Matrix spike percent recovery} = \frac{SSR - SR}{SA} \times 100\%$$

Where: SSR = Spiked sample results
SR = Sample results
SA = Spike added from spiking mix

The relative percent difference (RPD) between duplicate values for each component found in the sample is to be calculated using the following equation:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100\%$$

Where: D_1 = First sample value
D_2 = Second sample value (duplicate)

APPARATUS:

- Soxhlet extractors
- Erlenmeyer flasks, 250-mL to 500-mL Pyrex® glass
- Kuderna-Danish (K-D) apparatus consisting of 10-mL graduated (1-mL graduations) concentrator tubes, 500-mL evaporative flask, and three-ball macro snyder columns
- Pyrex glass wool, prerinsed with appropriate solvents to ensure its cleanliness

- Teflon® boiling chips, approximately 10/40 mesh
- Powder funnels, 65 mm x 108 mm with Whatman No. 4 filters
- Analytical balance, capable of accurately weighing ±0.0001 g
- Water bath, heated, with concentric ring cover, capable of temperature control (±2°C) (The bath should be used in a hood.)
- Muffle furnace, capable of operating at a temperature of up to 400°C
- Nitrogen evaporation device, N-Evap by Organomation Associates, Inc., South Berlin, MA
- Gas chromatograph system, complete with gas chromatograph and all required accessories including syringes, analytical columns, gases, electron capture detector, and stripchart recorder with recording integrator; a data system is required for measuring peak areas or peak heights and recording retention times

Note: Equivalent equipment may be substituted.

REAGENTS:

- Acetone, hexane, iso-octane, methanol, methylene chloride, petroleum ether, acetonitrile (all pesticide quality or equivalent)
- Sodium sulfate (ACS), granular, anhydrous, purified by heating at 400°C for 4 hours in a shallow tray
- Mercury

Note: Equivalent reagents may be substituted.

STANDARD PREPARATION:

Surrogate Spiking Solution

Prepare a 100-µg/mL solution of 2,4,5,6-tetrachloro-m-xylene (TMX) in methanol or acetone.

Matrix Spiking Solutions

Pesticide Spiking Solutions - The pesticide matrix spiking solutions should contain the following compounds at a concentration of 20 µg/mL in methanol, acetone, or iso-octane.

Hexachlorobenzene	Dieldrin
alpha-BHC	O,P'-DDE
gamma-BHC	O,P'-DDD
Oxychlordane	Endrin
Heptachlor epoxide	4,4'-DDT
alpha-chlordane	4,4'-DDD
Trans-nonachlor	4,4'-DDT
gamma-chlordane	Mirex
O,P'-DDE	Tetrachloro-m-xylene

Instrument Calibration Standards

1. Column Evaluation Standard - Prepare a mixed standard containing 0.1 µg/mL of 4,4'-DDT and endrin in hexane or iso-octane.

2. Individual Standard Mixtures - These include all single-component organochlorine pesticides. Two mixtures of the individual component standards are prepared to maximize resolution of those compounds on both columns to be used in the analysis. Prepare the two individual standard mixtures in hexane or iso-octane at the concentrations specified.

STANDARD MIX - 1

Pesticide	Conc. A	Conc. B	Conc. C
Hexachlorobenzene	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
gamma-BHC	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Oxychlordane	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
alpha-Chlordane	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
gamma-Chlordane	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
4,4'-DDE	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
4,4'-DDD	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
4,4'-DDT	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Endrin	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Tetrachloro-m-xylene	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL

STANDARD MIX - 2

Pesticide	Conc. A	Conc. B	Conc. C
alpha-BHC	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Heptachlor epoxide	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
trans-Nonachlor	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
O,P'-DDE	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
O,P'-DDD	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
O,P'-DDT	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Dieldrin	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Mirex	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Tetrachloro-m-xylene	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL

3. Multiresponse Pesticide and Beta-BHC Standard - Prepare the multiresponse pesticides in a single mixture containing the following compounds and concentrations in hexane or iso-octane.

Pesticide	Conc. A	Conc. B	Conc. C
Beta BHC	0.02 µg/mL	0.1 µg/mL	1.0 µg/mL
Toxaphene	0.2 µg/mL	1.0 µg/mL	10.0 µg/mL

4. PCB Stock Standards - Prepare stock solution of Aroclors 1242, 1248, 1254, and 1260 at concentrations of 20 µg/mL in hexane.

5. PCB Working Standards - Use the following dilution scheme for preparing working standards for the individual PCB Aroclors (note that all Aroclors must be prepared as separate standard solutions).

Conc. A	Conc. B	Conc. C
0.2 µg/mL	1.0 µg/mL	10.0 µg/mL

PROCEDURE:

Sample Preparation

1. Homogenize samples completely using either a blender or a Tekmar Tissuemizer®. Larger samples may need to be ground initially using a large meat grinder.

2. Clean equipment with soap and water and rinse it with acetone after each sample is ground.

Sample Extraction

1. Blend 10 g of ground tissue with 40 g of anhydrous sodium sulfate in a 250-mL beaker.

Note: If there is not 10 g of sample available then remove about 1 g for percent moistures (see step 5) and weigh the remainder for extracting. For wet samples more sodium sulfate may be required. If a sufficient amount has been added the sample will appear granular.

2. Add 100 µL of the pesticide spiking solution to the matrix spike and the control spike.

3. Add 20 µL of the TMX surrogate spiking solution to all samples and the method blank.

4. Allow the ground tissue/sodium sulfate to dry under a hood for a couple of hours, stirring it occasionally.

5. Place about 1 gram of sample onto a preweighed aluminum pan.

   5.1 Dry the sample at least 16 hours in an oven at 105°C.

   5.2 Weigh the pan and sample again after drying.

   5.3 Calculate the percent moisture as follows:

$$\% \text{ Moisture} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Wet weight}} \times 100\ \%$$

6. Load the prepared sample into the Soxhlet extractor between two plugs of preextracted glass wool.

   6.1 Place 250 mL of methylene chloride into a prerinsed 500-mL Erlenmeyer flask containing three to five Teflon boiling chips.

   6.2 Attach the flask to the extractor.

6.3 Add 100 mL of methylene chloride to the mixing beaker, swirl, and add the solvent to the extractor prior to attaching the condenser.

6.4 Adjust the temperature of the heating mantle so that the extractors cycle at a rate of 12 to 15 cycles per hour. Allow the system to cycle for 16 to 20 hours.

7. Allow the extract to cool after the extraction is complete. Rinse the condenser with extraction solvent and drain the Soxhlet apparatus into the bottom collection flask.

8. Pour the extract through a Whatman No. 4 filter into a 500-mL K-D flask fitted with a 10-mL concentrator tube. Attach a three-ball snyder column to the K-D flask and concentrate the extract on a hot water bath, adjusting the temperature so that the concentration is completed within 15 to 20 minutes.

9. When the apparent volume reaches approximately 5.0 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Bring up to a volume of 10 mL with methylene chloride.

Percent Lipids

Place 1 mL of the 10-mL extract into a preweighed aluminum weighing pan. Allow the pan to sit lightly covered in a hood overnight to allow the solvent to evaporate. Weigh the pan. Use the following equation to calculate the percent lipid.

$$\frac{\text{(Weight (g) of pan + lipid) - weight (g) of pan} \times 10\ \text{mL}}{\text{grams extracted}} \times 100\ \% = \%\ \text{lipid}$$

Extract Cleanup

1. Proceed with the appropriate cleanups as necessary (GPC; OP-6004-LP.001, Florisil cleanup for pesticides and PCBs; OP-6004-TLP.001 and OP-6004-LP.002, silica gel separation; OP-6004-TLP.003, and mercury shakeout to remove sulfur; OP-6004-DLP.004). All tissue samples should be cleaned using GPC. The sample extracts, after being exchanged to hexane, may be screened following GPC cleanup to determine if any additional cleanups such as Florisil may be needed or if silica gel separation may be required. It is recommended that all nonplant tissue extracts be separated using silica gel.

2. Take extract to a final volume of 2 mL in hexane (5 mL if sample was not GPC'd).

Instrumental Analysis

1. Recommended GC Columns and GC Operating conditions

1.1 Column 1: 30 m x 0.53-mm i.d., DB-608 Megabore
Inst conditions: INJ temperature 200°C, DET temperature 300°C
Temperature program: 180°C to 220°C at a rate of 1°C/minute,
220°C to 270°C at a rate of 5°C/minute,
hold for 5 minutes
Carrier gas: Helium at 6.5 mL/minute
Makeup gas: Nitrogen at 30 mL/minute

1.2 Column 2: 30 m x 0.53-mm i.d., DB-1701 Megabore
Inst conditions: INJ temperature 200°C, DET temperature 300°C
Temperature program: 180°C to 220°C at a rate of 1°C/minute,
220°C to 270°C at a rate of 5°C/minute,
hold for 5 minutes
Carrier gas: Helium at 6.5 mL/minute
Makeup gas: Nitrogen at 30 mL/minute

1.3 Column 3: 30 m x 0.53-mm i.d., DB-5 Megabore
Inst conditions: INJ temperature 200°C, DET temperature 300°C
Temperature program: 180°C to 220°C at a rate of 1°C/minute,
220°C to 270°C at a rate of 5°C/minute,
hold for 5 minutes
Carrier gas: Helium at 6.5 mL/minute
Makeup gas: Nitrogen at 30 mL/minute

2. Instrumental Analysis

All extracts are analyzed using GC-EC. The sample extracts are analyzed and compared with external standards for qualitative and quantitative purposes. If the extract has been separated into a pesticide and a PCB fraction using silica gel, then each fraction is analyzed only for those analytes expected in the fraction.

3. Pesticide Analysis

3.1 The pesticides are analyzed on a gas chromatograph with wide-bore capillary columns and an electron capture detector. An initial injection of an evaluation mixture containing 4,4'-DDT and endrin is made. Breakdown of the 4,4'-DDT into 4,4'-DDD and 4,4'-DDE and/or endrin into endrin ketone and endrin aldehyde must not exceed 20%. The percent breakdown is calculated using Equation 1.0. If the breakdown for either 4,4'-DDT or endrin does exceed 20%, the run cannot be used for analysis of samples.

Equation 1.0:

$$\%\text{DDT Breakdown} = \frac{\text{Area of 4,4'-DDD + 4,4'-DDE}}{\text{Area of 4,4'-DDT + 4,4'-DDD + 4,4'-DDE}} \times 100\ \%$$

$$\%\text{Endrin Breakdown} = \frac{\text{Area of endrin aldehyde + endrin ketone}}{\text{Area of endrin + endrin aldehyde + endrin ketone}} \times 100\%$$

3.2 A three-point calibration of the Aroclors and the pesticide Standard Mixes A, B and C are analyzed prior to sample analysis. The correlation coefficient of the linear regression of the three-point standards and zero must be greater than 0.995 for each analyte in order to be able to quantitate.

3.3 Five samples may be analyzed followed by another injection of the evaluation mixture. The evaluation mixture must continue to exhibit less than 20% breakdown of 4,4'-DDT and endrin.

3.4 Five more samples may be analyzed followed by an injection of one of the B pesticide standards and either the beta-BHC/toxaphene or one of the Aroclor B standards. The peak areas of the analytes in each ongoing B standard must be within 20% of the peak areas of the same initial standard. The sequence of samples, the evaluation mixture, and the B standards may continue as long as the acceptance criteria are met. The last sample injection must be followed by an injection of all B pesticide standard mixes.

3.5 If any standard does not meet the acceptance criteria, then that standard and any samples analyzed after it, may be reinjected. If the standard is still unacceptable, the analytical run is completed with that standard and a new initial calibration must be run in order to analyze more samples.

Analytical Sequence

1	Evaluation Mixture
2	Aroclor 1242-A
3	Aroclor 1242-B
4	Aroclor 1242-C
5	Aroclor 1248-A
6	Aroclor 1248-B
7	Aroclor 1248-C
8	Aroclor 1254-A
9	Aroclor 1254-B
10	Aroclor 1254-C
11	Aroclor 1260-A
12	Aroclor 1260-B
13	Aroclor 1260-C
14	Beta-BHC/Toxaphene A
15	Beta-BHC/Toxaphene B
16	Beta-BHC/Toxaphene C
17	Standard Mix 1-A
18	Standard Mix 1-B
19	Standard Mix 1-C
20	Standard Mix 2-A
21	Standard Mix 2-B
22	Standard Mix 2-C
23 - 27	Five samples
28	Evaluation Mixture
29 - 33	Five samples
34	Standard Mix 1-B or 2-B
35	Beta-BHC/Toxaphene-B or one of the Aroclor-B
36	Repeat Steps 23 through 35 ending the sequence with the three B pesticide standards.

3.6 Retention time windows (RTWs) of each analyte are established as follows.

3.6.1 Analytes eluting prior to 14 minutes have an RTW of ±0.07 minutes of the initial B standard retention time. For example, a peak with an initial retention time of 10 minutes has a RTW of 9.93 to 10.07 minutes.

3.6.2 The RTW for any analytes eluting later than 14 minutes, but prior to 20 minutes, will be 0.6% of the initial B standard retention time. For example, a peak with an initial retention time of 17 minutes has a window of 16.90 to 17.10 minutes.

3.6.3 The RTW for analytes eluting 20 minutes or later will be established as ±0.5% of the initial B standard retention time. The retention times for the ongoing standards must fall within their respective RTW in order to continue sample analysis.

NOTE: The sample peaks being analyzed must be within the calibration range of the initial standards. A peak is qualitatively identified if the retention time falls within the RTW established for an analyte of interest.

3.7 The tentatively identified sample peak is quantified using Equation 1.1.

Equation 1.1

Tissue: $\frac{(A_1)\ (C)\ (V)\ (D)}{(A_2)\ (M)} = \mu g/kg$

Where:
- A_1 = Area of sample peak
- A_2 = Area of Midpoint Standard peak
- C = Concentration of Midpoint Standard (µg/mL)
- V = Extract volume (mL)
- D = Dilution factor
- M = Mass of sample extracted (kg)

3.8 Confirmation (Second column)

3.8.1 Second-column confirmation is qualitative only, therefore only the injection of a midpoint standard is required; however the evaluation mixture containing DDT and Endrin must also be injected and it must demonstrate that the column breakdown of those two compounds do not exceed 20%.

3.8.2 The peak of interest must fall within the RTW on the second column to be confirmed. However, the analyst's judgment may also be used in deciding if a peak does or does not confirm.

3.8.3 The confirmation run may be used to quantitate compounds found in the sample if coeluting peaks encountered in the primary quantitation run interfere with accurate quantification. If the confirmation run is used as a "secondary quantitation run" for selected compounds, this use must be noted and those compounds quantitated on the run documented. In those cases where quantitation is performed, all relevant calibration criteria will apply for those compounds to be quantified including: initial calibration, continuing calibration and DDT/Endrin breakdown.

4. PCB Analysis

4.1 The individual PCBs are identified by pattern recognition. Individual PCB quantification is done by summing the areas of at least five sample peaks and also summing the same five peaks in the initial standard closest in area to the sample (for example, the A standard of Aroclor 1242, if the amount of Aroclor 1242 in the sample is near the detection limit). These area sums are used in Equation 1.1 to calculate the concentration of PCBs present in the sample.

4.2 Total PCB's are obtained by summing the individual Aroclors quantified.

Mass Spectrometry Confirmation

1. Ten percent of the samples and at least one sample per matrix must be analyzed by gas chromatography/mass spectroscopy (GC/MS) if any of the samples in a set confirm for any analyte that has a concentration in the extract greater than 10 ng/μL. The blank associated with any samples requiring GC/MS confirmation must also be analyzed. At least one standard of any analyte being confirmed must be injected prior to and after analysis of the samples. The results presented on the Sample Result Form must state if the GC/MS confirmation was required for the sample and if the analytes of interest confirmed.

2. If an analyte appears to be present, based on electron capture gas chromatography, at a concentration higher than the limit of detection for mass spectrometry, and the identity of that compound can not be confirmed or tentatively confirmed by mass spectrometry, it should be assumed that the electron capture result is due to an interference. The report should be adjusted (for all samples controlled by the mass spec sample in question) to read < the former result. The detection limit is redefined as the apparent concentration due to the interference.

Documentation and Reporting

Follow all general standard operating procedures for the complete documentation of all standard and sample preparation as well as instrumental analysis and analyte calculations. Raw data and hardcopies of the results must be filed. A cover letter, a diskette summary of the results, and a Matrix Spike Recovery and Duplicate Analysis Form will be sent to the client.

Hazleton Environmental Services

QAU - DO NOT DUPLICATE

MP-FWST-MA
Attachment 1

Method Detection Limits (MDLs)

Compound	Validation MDL (µg/kg)	Standard Reporting Detection Limit (µg/kg)
4,4'-DDE	2.6	10.0
4,4'-DDD	4.0	10.0
4,4'-DDT	2.3	10.0
4,4'-DDE	7.2	10.0
4,4'-DDD	5.2	10.0
4,4'-DDT	6.2	10.0
Hexachlorobenzene (HCB)	8.9	10.0
Technical BHC	8.0	10.0
alpha-BHC	1.6	10.0
gamma-BHC	1.1	10.0
Dieldrin	11.0	10.0
Heptachlor epoxide	1.5	10.0
Oxychlordane	1.6	10.0
alpha-Chlordane	3.6	10.0
gamma-Chlordane	5.9	10.0
trans-Nonachlor	2.8	10.0
Endrin	6.7	10.0
Mirex	3.9	10.0
Toxaphene	10.0	50
PCB-1242	12.0	50
PCB-1248	27.0	50
PCB-1254	30.0	50
PCB-1260	10.0	50

Note: Validated MDLs determined according to the protocol outlined in 40 CFR 136, Appendix B, October 26, 1984, Definition and Procedure for the Determination of the Method Detection Limit.

Hazleton Environmental Services

QAU - DO NOT DUPLICATE

3 4 0212

MP-FWST-MA
Attachment 2

Method Performance
Organochlorine Pesticides/PCBs
Tissue Matrix

Compound	CAS No.	MDL µg/kg	Average % Recovery	% Relative Deviation	Windows
4,4'-DDE	72-55-9	2.6	94	10	73 - 114
4,4'-DDD	72-54-8	4.0	104	16	71 - 136
4,4'-DDT	50-29-3	2.3	97	12	73 - 121
O,P'-DDE	3424-82-6	7.2	91	9.5	72 - 110
O,P'-DDD	53-19-0	5.2	90	15	61 - 119
O,P'-DDT	789-02-6	6.2	88	9.7	69 - 108
HCB	118-74-1	8.9	92	9.3	74 - 111
alpha-BHC	319-84-6	1.6	82	12	57 - 106
gamma-BHC	58-89-9	1.1	84	9.8	64 - 104
Dieldrin	60-57-1	11.0	90	12	67 - 114
Heptachlor epoxide	1024-57-3	1.5	86	11	64 - 107
Oxychlordane	27304-13-8	1.6	92	13	66 - 118
alpha-Chlordane	5103-71-9	3.6	88	12	63 - 112
gamma-Chlordane	5103-74-2	5.9	92	11	69 - 115
trans-Nonachlor	39765-80-5	2.8	96	13	71 - 122
Endrin	72-20-8	6.7	98	9.2	80 - 117
Mirex	2385-85-5	3.9	90	14	63 - 118
Toxaphene*	8001-35-2	10.0	67	14	48 - 86
PCB-1242	53469-21-9	12.0	89	14	61 - 117
PCB-1248*	12672-29-6	27.0	116	17	82 - 150
PCB-1254	11097-69-1	30.0	102	29	44 - 160
PCB-1260	11096-82-5	10.0	ND	ND	ND

ND = Not Determined
* Statistics reflect a limited number of data points.

Hazleton Environmental Services

Addendum to FWST for SAS 7987-A

We propose the following be incorporated into our FWST method for use in the analysis of samples for SAS 7987-A:

- We will add methoxychlor and chlorpyrifos as analytes of interest to the FWST method. Standards for chlorpyrifos will be analyzed at the same concentrations as the other single response analytes. The standards for methoxychlor will be analyzed at 10X the level of the other single response analytes.

- Chlorpyrifos will be added to the spikes at the same level as the other single response analytes. Methoxychlor will be added at 10X the amount of the other analytes of interest.

- The analytes which are listed in our FWST method, but are not requested in the bid, will not be analyzed for.

- We will not confirm analytes of interest by GC/MS for this SAS.

- This bid requests the analysis of "total PCBs" but the specific Aroclors are not listed. Our FWST method requires that total PCBs be obtained by summing the individual Aroclors quantified in the sample. The FWST method requires the analysis of Aroclors 1242, 1248, 1254, and 1260 since these are the Aroclors expected to be found in the envinronment, in particular in tissues. We propose to continue analyzing for these four Aroclors. If other Aroclors are required (eg. 1221, 1232, and 1016) we could analyze them in this method but our experience with analyzing thousands of fish samples specifically for PCBs is that these other Aroclors are typically not present in tissue samples.

MERCURY ANALYSES IN WATER (FRONTIER GEOSCIENCES LOW DETECTION LIMIT METHOD)

Total and "Acid-Labile" Mercury in Aqueous Media

1.0 SCOPE AND APPLICATION

1.1 Our methodology is a peer-reviewed, published procedure for the determination of total mercury in a wide range of aqueous samples, ranging from pristine seawater to sewage effluent.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the aqueous samples must be prepared according to the procedure discussed in this method.

2.2 Cold vapor atomic fluorescence is based upon the emission of 253.7 nm radiation by excited Hg^0 atoms in an inert gas stream. Mercuric ions in the oxidized sample are reduced to Hg^0 with $SnCl_2$, and then purged onto gold-coated sand traps as a means of preconcentration and interference removal. Mercury vapor is thermally desorbed to a second ("analytical") gold trap, and from that into the fluorescence cell. Fluorescence (peak height or area) is measured as a function of total mercury collected, which is converted to concentration by the size of the aliquot purged.

2.3 The typical detection limit for the method is 0.002 $ng \cdot L^{-1}$ for "acid-labile" mercury and 0.05 $ng \cdot L^{-1}$ for total mercury.

3.0 INTERFERENCES

3.1 Due to the BrCl oxidation step, there are no observed interferences with the total Hg methodology when properly carried out. The "acid-labile" mercury technique, however, is operationally quantifying an interference, i.e.; the partial complexation of Hg by organic matter. Thus it is critical to follow the instructions for standardization accurately. Also, when "acid-labile" Hg samples are analyzed, most of the Hg may be in non-labile forms, which then can adsorb to the bubbler walls. It is critical, therefore, to clean the bubblers at least daily, and always between "acid labile" and total mercury determinations as described below. FAILURE TO DO SO WILL RESULT IN CARRY-OVER

OF MERCURY AND IRREPRODUCIBLE RESULTS. This problem does not exist during the analysis only of total mercury samples. The cleaning procedure is as follows:

a) Fill bubblers with 10% KOH in water, and let sit for 10 minutes.
b) Fill bubblers with concentrated HCl, and bring to boil in fume hood. Heat with HCl for 30 minutes.
c) Fill bubblers with clean deionized water plus 1 mL of BrCl solution. Let sit for 10 minutes.
d) Neutralize BrCl with 0.5 mL NH_2OH solution, discard, and rinse the entire bubbler apparatus with copious quantities of ultra-pure water.
e) Fill with 1% HCl and purge with N_2 at about 25 $mL \cdot min^{-1}$ until further use.

3.2 The potential exists for destruction of the gold traps (and consequently low values) if free halogens are purged onto them, or if they are overheated (>500 C). When these instructions are followed accurately, neither of these outcomes is likely.

3.3 Water vapor may collect in the gold traps and be released into the fluorescence cell where it condenses, giving a false peak due to scattering of the excitation radiation. This can be avoided with the gold trap pre-drying step, and by discarding traps which tend to absorb large quantities of water vapor.

3.4 As always with atomic fluorescence, the fluorescent intensity is strongly dependent upon the inertness of the carrier gas. The dual amalgamation technique eliminates quenching due to trace gases, but it still remains the analyst's responsibility to ensure high purity inert carrier gas and a leak-free analytical train.

4.0 APPARATUS AND MATERIALS

4.1 Atomic fluorescence spectrophotometer or equivalent. To achieve the low detection levels and small, interference-free sample aliquots claimed by this method, a very sensitive CVAFS detector is required. Such systems can be

built in-lab according to Bloom and Fitzgerald (1988). Other mercury specific detectors such as atomic absorption or plasma emission may be used, but detection limits would be 10-100 times higher. The CVAFS detector contains the following four major components:

4.1.1 Four-watt low pressure mercury vapor lamp.

4.1.2 Far UV quartz flow-through fluorescence cell 12 mm x 12 mm x 45 mm long, with a 10 mm path length.

4.1.3 UV-visible photomultiplier: sensitive to <230 nm. This PMT is isolated from outside light with a 254 nm interference filter.

4.1.4 Flowmeter: flowmeter with needle valve capable of reproducibly keeping carrier gas flow at 30 $mL \cdot min^{-1}$.

4.2 Flow meter/needle valve: capable of controlling and measuring gas flow to the purge vessel at 200-500 $mL \cdot min^{-1}$.

4.3 Teflon fittings: Connections between components and columns are made using 6.4 mm O.D. teflon FEP tubing, and teflon friction-fit or threaded tubing connectors. Connections between components requiring mobility are made with 3.2 mm O.D. teflon tubing due to its greater flexibility.

4.4 Acid fume pre-trap: A 10 cm x 0.9 cm diameter teflon tube containing 2-3 grams of reagent grade, non-indicating 8-14 mesh soda lime chunks, packed in between wads of silanized glass wool. This trap is purged of Hg by placing on the output of a clean cold vapor generator, filled with 1% HCl in water, and purging overnight with N_2 at 100 $mL \cdot min^{-1}$.

4.5 Cold vapor generator: a 250 mL or 125 mL Florence flask with standard taper 24/40 neck, fitted with a spurging stopper having a coarse glass frit which extends to within 0.2 cm of the flask bottom.

4.6 Gold-coated sand columns: Made from 10 cm lengths of 6.5 mm O.D. x 4 mm quartz tubing, with a coarse quartz frit 2.0 cm from one end. The tube is filled with 3.4 cm of gold-coated ashed (800 C for 6 hours) quartz sand (60/80 mesh). The end is then plugged with quartz wool. Gold is applied to the sand as a coating several atoms thick using an ion discharge gilding apparatus such as is employed to coat electron microscopy samples. Columns are heated to

450-500 C (a barely visible red glow when the room is darkened) with a coil consisting of 75 cm of 24 ga Nichrome wire at a potential of 10 VAC. Potential is applied and finely adjusted with an auto transformer.

4.7 Recorder: Any multi-range chart recorder or integrator with 0.1-5.000 mV input and variable speeds is acceptable.

4.8 Pipetters: All plastic pneumatic fixed volume and variable pipetters in the range of 10 uL to 5.0 mL.

4.9 Sampling and Oxidation Bottles: It is imperative for accurate $ng \cdot L^{-1}$ mercury work that appropriately cleaned teflon bottles with tight-fitting lids be used for all steps contacting the aqueous sample. It is good practice to use 1000 mL or 500 mL bottles to collect the samples in, and 125 mL bottles to perform the BrCl oxidation step. New teflon bottles are cleaned by heating to >95 C in concentrated HNO_3 for at least 48 hours. The bottles are cooled, rinsed 3 times with ultra-clean water, and then filled with ultra-clean water containing 1% HCl. These bottles are capped and placed in a clean oven at 50 C overnight. After cooling, they are rinsed 3 more times, filled with ultra-pure water plus 1% HCl, and placed in a mercury-free class 100 clean-air station until dry. The bottles are then tightly capped (with a wrench) and double bagged in new polyethylene zip-loc bags until needed. After the initial cleaning, bottles are cleaned by heating c.a. 6 hours in HNO_3, rinsing 4 times, and filling with high purity 1% HCl solution.

5.0 REAGENTS

5.1 Water: 18 megohm ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. As a final mercury and organic removal step, the activated carbon cartridge on the 18 megohm system is placed between the final ion exchange bed and the 0.2 uM filter. Water should be monitored for Hg--especially after ion exchange beds are changed.

5.2 Air: For best results doing low level aquatic mercury research, it is very important that the laboratory air be low in both particulate and gaseous mercury. This is generally not the case for existing laboratories, as years of

broken thermometers, use of Hg salts as reagents, and mercury preserved paints on the walls have permanently elevated room air levels to hundreds of $ng \cdot m^{-3}$. Ideally, mercury work should be conducted in a new laboratory, with mercury-free paint on the walls. Outside air, which is very low in Hg should be brought directly into the class-100 clean air station intakes. If this is impossible, air coming into the clean air stations can be cleaned for mercury by placing a gold-coated cloth pre-filter over the intake. This is made as follows:

> Soak several square meters of cotton gauze in 100 mL of 10% gold chloride solution at pH 7. In a hood, add 100 mL of 30% NH2OH.HCl solution, and homogenize into the cloth with gloved hands. The material will turn black as colloidal gold is precipitated. Allow the mixture to sit for several hours, then rinse with copious amounts of deionized water. considerable colloidal gold will be washed out, so you may wish to collect and settle the rinse water to recover it. Squeeze dry the rinsed cloth, and spread flat on newspapers to air-dry. When dry, fold and place over the intake pre-filter of your laminar flow hood. CAUTION: THIS PROCESS IS MESSY, SO GREAT CARE SHOULD BE TAKEN TO AVOID SPREADING GOLD DUST THROUGHOUT THE LABORATORY. THIS COULD CAUSE INTERFERENCES WITH ANALYSIS IF GOLD BECOMES INCORPORATED IN THE SAMPLES. THE GILDING PROCEDURE SHOULD BE DONE IN A REMOTE LABORATORY IF AT ALL POSSIBLE.

5.3 Hydrochloric acid. Trace-metal purified reagent HCl is purchased and pre-analyzed for Hg before use. In general, it is possible to obtain acid containing less than 5 $pg \cdot mL^{-1}$ Hg. When a lot number meeting this specification is found, several cases are purchased, and stored in a low Hg atmosphere (i.e.; in clean lab or outside the building). Generally lower values can be obtained in this manner, than by re-distilling acid in the laboratory. So called ULTRA-PURIFIED acids are often the most irreproducibly contaminated (for mercury) grade of acid commercially available and should be avoided.

5.4 Hydroxchlorine Hydrochloride. Dissolve 300 grams of $NH_2OH \cdot HCl$ in ultra-pure water to make 1.0 L. This solution may be purified by the addition

of 1.0 mL of $SnCl_2$ solution and purging overnight at 500 $mL \cdot min^{-1}$ with Hg-free N_2.

5.5 Stannous chloride. A solution containing 200 g of $SnCl_2 \cdot 2H_2O$ and 100 mL concentrated HCl is brought to 1.0 L with high purity water. This solution is purged overnight with mercury-free N_2 at 500 $mL \cdot min^{-1}$ to remove all traces of Hg. Store tightly capped, and in the dark.

5.6 Bromine monochloride. 27 g of KBr are added to a 2.5 L bottle of concentrated HCl analyzed and found to be low in Hg (<5 $ng \cdot L^{-1}$). A clean magnetic stir bar is placed in the bottle, and it is stirred for 1 hour, in a fume hood. Next, 38 g of pre-analyzed, low Hg $KBrO_3$ are slowly added to the acid with stirring. When all of the $KBrO_3$ has been added, the solution should have gone from yellow to red to orange. Loosely cap the bottle, and allow to stir another hour before tightening the lid. CAUTION: THIS PROCESS GENERATES COPIOUS QUANTITIES OF FREE HALOGENS (Cl_2, Br, BrCl) WHICH ARE RELEASED FROM THE BOTTLE. ADD THE $KBrO_3$ *SLOWLY* AND IN A WELL OPERATING FUME HOOD!

5.7 Stock mercury standard: A commercially available 1000 $mg \cdot L^{-1}$ mercury atomic absorption standard is commonly used. Alternatively, 0.1354 g of high purity $HgCl_2$ may be dissolved in 75 mL of water, 5 mL of bromine monochloride solution added, and the volume brought to 100.0 mL in a class A volumetric flask.

5.8 Mercury secondary standard solution: 0.100 mL of the stock solution is diluted to 100.0 mL of water containing 5 mL of bromine monochloride. This solution contains 1.00 $ug \cdot mL^{-1}$ Hg. Keep in a tightly closed teflon bottle. This solution should be replaced or re-standardized yearly.

5.9 Mercury working standard. 1.00 mL of the mercury secondary standard is diluted to 100.0 mL in a class A volumetric flask with high purity water containing 1% by volume bromine monochloride solution. This solution contains 10.0 $ng \cdot mL^{-1}$ and should be replaced monthly.

5.10 Nitrogen: Grade 4.5 (standard laboratory grade) nitrogen which has been further purified by the removal of Hg using a gold-coated sand trap.

5.11 Helium or Argon. Grade 5.0 (ultra-high purity, G.C. grade) inert gas which has been further purified by the removal of Hg using a gold-coated sand trap.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples should be collected only into rigorously cleaned teflon bottles. Under no circumstances should ordinary plastic (i.e.; polyethylene, polypropylene or vinyl) containers be used, as they are very diffusive to Hg gas from the air. Ashed or rigorously acid cleaned Borosilicate or quartz glass bottles with teflon caps may be used as well. It is critical that the bottles have very tightly sealing caps to avoid diffusion of atmospheric Hg through the threads (Gill and Fitzgerald, 1985). As an added precaution, clean bottles, filled with high purity 1% HCl are dried, capped, and double bagged in new zip-loc bags in the clean room, and stored in wooden or plastic boxes until use.

6.2 Samples are collected using rigorous ultra-clean protocols (Gill and Fitzgerald, 1985) which are summarized as follows:

a) At least two persons, wearing fresh clean-room gloves at all times, are required on a sampling crew.
b) One person ("dirty hands") pulls a bagged bottle from the box, and opens the outer, dirty bag, avoiding touching inside that bag.
c) The other person ("clean hands") reaches in, opens the inner bag, and pulls out the sample bottle.
d) This bottle is opened with a plastic shrouded dedicated wrench, and the acidified water is discarded downstream of the sampling site.
e) The bottle is rinsed once with sample water, and then filled.
f) Preservative (i.e.; 5% by volume of high purity HCl) may be added at this time, or within several hours at the clean laboratory.
g) The cap is replaced with the wrench, and the bottle re-bagged in the opposite order from which it was removed.
h) Clean-room gloves are changed between samples and whenever something not known to be clean is touched.

i) Water samples are best obtained by surface grab, using gloved hands, and facing into a flowing body of water (i.e.; looking upstream or off the bow of a moving boat). If samples are to be taken from depth, the only non-contaminating method generally available is pumping. Two methods have been found to work in this regard. The first is to use rigorously acid-cleaned teflon tubing, and a peristaltic pump with FRESHLY cleaned (heating to 70 C in 5% HCl + 5% CH_3OOH) silicone tubing. Beware that once cleaned, silicone tubing quickly absorbs Hg from the air. The other method involves high-volume pumping (i.e.; 50 $L \cdot min^{-1}$) through neoprene hose. If this method is used, it is best to clean the system first by pumping several hundred liters of 5% HCl solution, and then pumping clean water for several hours. This second technique works largely because the rate of flow is so fast that the contamination becomes imperceptibly diluted.

j) DISCRETE SAMPLERS, i.e.; Niskin, GoFlo, and Kemerer BOTTLES ARE TO BE AVOIDED, AS, UNDER EVEN THE BEST OF CONDITIONS THEY ARE OFTEN FOUND TO GROSSLY CONTAMINATE SAMPLES AT THE $NG \cdot L^{-1}$ LEVEL.

6.3 Samples may be preserved by adding 5 $mL \cdot L^{-1}$ of concentrated HCl (to allow both "acid-labile" and total mercury analysis) or 5 $mL \cdot L^{-1}$ BrCl solution, if only total mercury is to be analyzed. Samples may also be sent back to the laboratory unpreserved if they are 1) collected in teflon bottles, 2) filled to the top with no head space, and 3) send at 1 C by overnight mail The samples should be acid preserved soon after arrival at the laboratory (within 24 hours). FREEZING IS NOT AN ACCEPTABLE TECHNIQUE FOR TOTAL Hg, AS UPON THAWING, MUCH Hg(II) IS CONVERTED TO VOLATILE Hg^0.

6.4 All handling of the samples in the lab should be undertaken in a mercury-free clean air bench, after rinsing the outside of the bottles in low Hg water, and drying in the clean air hood.

7.0 PROCEDURE

7.1 Sample Preparation. The value obtained for "acid-labile" mercury is somewhat dependent upon the length of time the sample is stored with acid. The amount of "acid-labile" mercury recovered levels off after about 3 weeks of aging, at a level which may be twice that observed in a fresh sample. Thus, greatest reproducibility is obtained by storage for 1 month before analysis, but this is often not feasible. Currently no uniform protocol exists clearly defining the acidification parameter for "acid-labile" Hg. For total Hg, a 100 mL aliquot should be poured from a thoroughly shaken, acidified sample, into a 125 mL teflon bottle. 0.5 mL of BrCl are added, the bottle capped, and allowed to digest for at least 1 hour. If the yellow color disappears due to consumption by organic matter or sulfides, more BrCl should be added until a permanent yellow color is obtained. Some highly organic matrices such as sewage effluent will require high levels of BrCl (ie; 5 mL·100 mL^{-1} of sample), and longer oxidation times, or elevated temperatures (ie; place sealed bottles in oven at 50 C for 6 hours). In all cases, the oxidation must be conducted until a permanent yellow color remains.

7.2 Analysis: 100 mL of water is placed in each bubbler, and 1.0 mL of $SnCl_2$ is added. The bubbler is purged with Hg-free N_2 for 20 minutes at 300-400 $mL \cdot min^{-1}$. A gold/sand trap is then connected to the output of the soda lime pre-trap, and the water purged another 20 minutes to obtain a bubbler blank. Standards are then analyzed by the addition of 0.1-5.0 ng aliquots of Hg standard, and 0.5 mL $SnCl_2$ to the bubblers, swirling to mix, and purging as above.

For "acid-labile" mercury, place 100-200 mL of acidified sample into a clean bubbler, determining the volume by weight difference. Add 0.5 mL of $SnCl_2$ solution, replace the bubbler cap, and swirl to mix. Place a clean gold/sand column on the output of the soda-lime trap and purge for 20 minutes with Hg-free N_2 at 300-400 $mL \cdot min^{-1}$.

Please note that "acid-labile" Hg is an operationally defined fraction of the total, and hence the bubbling time is a defining parameter. The longer the sample is bubbled, the greater the amount recovered will be. Thus, reproducibility in the bubbling time is critical. Also, since most of the total Hg remains in the sample after bubbling, multiple samples must not be added to the same water in the bubbler -- ie; the bubbler must not be completely emptied between samples. SAMPLES TOO SMALL TO FILL THE BUBBLER

ABOVE THE FRIT, AND STANDARDS, MUST BE RUN ON $SnCl_2$ PURGED DEIONIZED WATER -- NOT ON TOP OF PURGED NATURAL WATER SAMPLES!

Total mercury may be analyzed after acid-labile values have been run only after cleaning the bubblers as described in section 3.1. To the BrCl oxidized sample in the 125 mL teflon bottles, 0.2 mL of 30% NH_2OH is added, the bottle capped, and the sample swirled. The yellow color will disappear, indicating the destruction of the BrCl. The sample is allowed to react for 5 minutes to be sure that no trace of halogens remain. PURGING OF FREE HALOGENS ONTO THE GOLD TRAPS WILL RESULT IN DAMAGE, AND LOW IRREPRODUCIBLE RESULTS THEREAFTER. Once the sample has been pre-reduced with NH_2OH, it may be analyzed as described for acid-labile Hg. When running total mercury samples, however, the recovery is quantitative, and organic interferents are destroyed. Thus standards and bubbler blanks may be run directly on top of past purged samples.

To analyze the mercury contained on a gold column, the Nichrome wire coil is placed around the column, and the column is inserted in the analyzer train between the incoming Hg-free helium and the second ("analytical") gold-coated sand column. Helium is allowed to pass through the column at a setting of about 30 $mL \cdot min^{-1}$ for 2 minutes to dry off condensed water vapor. Electrical current (10 VAC) is then applied to the coil for 4 minutes, thermally desorbing the Hg as Hg^0, which is carried by the He to the analytical gold column. After 4 minutes, the Nichrome coil is turned off, and a cooling fan directed toward the hot column. Next, the power to the Nichrome wire coil around the analytical column is turned on, as is the integrator or other data acquisition device. This column is heated for 3 minutes, or 1 minute beyond the point that the peak returns to baseline.

Following the recording of the peak, the analytical trap coil is turned off, and the cooling fan directed at it. The sample trap is now removed from the gas stream, and the teflon end plugs replaced until needed to collect another sample. The next sample column is placed in line, and the procedure repeated. Under no circumstances should a sample column be heated while the analytical column is still warm, or analyte may be lost by passing through the analytical column.

Peaks generated using this technique should be very sharp and almost symmetrical. The peak comes off at approximately 1 minute, and has a half-

height width of about 5 seconds. Broad or asymmetrical peaks are indicative of an analytical problem, possible including: low gas flow, water vapor on the column, or an analytical column damaged by chemical fumes or overheating. The last possibility is definitely the case if following a sharp peak, a secondary small broad peak is observed. If the analytical column has been damaged, it and the teflon tubing downstream from it should be discarded, due to the possibility of gold migration on downstream surfaces.

7.3 Cold Vapor Atomic Fluorescence for mercury is linear over at least 5 orders of magnitude (Bloom and Fitzgerald, 1988). However, it is recommended that a 3 point calibration curve, bracketing the analyte concentrations be prepared each day prior to analysis, to verify linearity.

7.4 Blanks: Blanks must be quantified from a variety of sources, and summed for most accurate results. The blank due to the preservative acid may be quantified by analyzing 1 mL of HCl as an "acid-labile" Hg sample. Bubbler blanks are quantified by purging previously purged deionized water. $SnCl_2$ blanks may be quantified by analysis of 5 mL of $SnCl_2$ as an "acid-labile" mercury sample. BrCl blanks are determined by pipetting 1.0 mL of BrCl directly into a previously purged oxidized water sample. 0.4 mL of NH_2OH solution and 0.5 mL of $SnCl_2$ are added, and the sample purged as a total Hg sample. To calculate the blanks then, all values have the mean bubbler blanks for a run subtracted, and then the reagent contribution is subtracted based upon the quantity of reagents calculated to be in the sample aliquot. For example, if a 1 litre sample was preserved with 5.0 mL of HCl containing 3 pg $Hg \cdot mL^{-1}$ acid, and 175 mL of this were analyzed, then the HCl reagent blank would be (175/1000)(5.0)(3.0) = 2.6 pg Hg from the acid. This is important because the bubbler blanks vary from day to day, but the reagent blanks only vary from batch to batch.

7.5 For total Hg, this methodology is virtually interference free, so the method of standard additions is not routinely applied. Spike recoveries should be performed at least every 20 samples however, as a check of analytical Q.C. "Acid-labile" mercury is an operational definition, so that both standard additions and spike recoveries are meaningless. The acid labile values can only be calibrated against total Hg standards.

7.6 Gold-coated sand columns should be kept track of by unique identifiers, so that any trap producing poor results can be quickly recognized and discarded. Occasionally due to inadvertent contact with halogen fumes, bubbler solution, organic fumes, or overheating, a sampling column will become damaged; giving low and irreproducible results. Suspect columns should be checked with at least 2 consecutive standard runs before continued use.

7.7 The major cause of analytical problems with this method is from using the soda lime pre-traps too long. These traps should be purged overnight as described and then used for only one day's analytical work. Longer use risks irreproducibility, as the traps may begin retarding the flow of Hg^0. Also, as they become very wet, there is a risk of NaOH-saturated water drops coming out onto the gold trap.

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed, as discussed in section 8.

7.9 Calculations may be made by reading off of the (linear) standard curve, or by the following method, which is functionally the same:

a) For each net standard result (peak height of standard minus mean peak height of bubbler blanks), divide by the ng of Hg in that spike, to yield the "peak height/ng Hg". Pool all of the "peak height/ng Hg" values for a given sample run when these results are statistically the same, to obtain a mean "peak height/ng Hg" value (A). A is also equal to the slope of the regression of the standard curve.

b) Pool the bubbler blank values to obtain a mean "peak height/aliquot of the bubbler blank (B).

c) Pool the contribution of reagent blanks (preservative acid, BrCl, etc.) on a per mL of reagent basis, forming a mean ng Hg per mL value (R).

d) Calculate the fraction of a mL of reagents in the particulate sample being analyzed (F). For example, if 0.5 mL of BrCl is in the sample analyzed, F = 0.5

e) To calculate the concentration of total mercury in a sample, employ the following formula:

$$\text{Hg ng.L-1} = \frac{[(S-B)/A]-FR}{V}$$

where V is the volume of the sample in L, and S is the gross sample peak height.

f) The detection limit is considered to be 3 times the standard deviation of the sum of the reagent blanks.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration data must be composed of a minimum of 3 blanks and 3 standards. Such a calibration should be run at least once per day, or every 20 samples, whichever comes first.

8.3 Samples containing high analyte concentrations may be run either following dilution, or on a separate run at lower instrumental sensitivity.

8.4 A minimum of 3 procedural blanks per batch of 20 samples must be run to obtain a meaningful value for the reporting limits of detection.

8.5 Duplicate or triplicate analyses (depending upon client preference) should be run once every 10 samples or once per batch, whichever comes first.

8.6 No certified materials exist for Hg in water near ambient levels. NRCC or NBS certified standards for mercury in solid matrices should be used as a QA/QC measure in lieu of these. In addition, intercalibration exercises with noted Hg research laboratories should be undertaken on ambient level water samples once each year.

9.0 METHOD PERFORMANCE

The data shown in Table 1 indicate the performance of the method under actual operating conditions by several different analysts. In addition to such data the methodology has been inter compared with other techniques for low level mercury determination in water under a variety of studies, including ICES-5 (Cossa and Couran, 1990), and an ongoing USGS QA/QC study at higher ($ug \cdot L^{-1}$) concentrations.

Table 1. Recovery of Hg_t from various unfiltered water types, using BrCl cold oxidation and dual gold amalgamation, with CVAFS detection (August, 1989).

	Total Mercury Concentrations, $ng \cdot L^{-1}$ as Hg				
Sample Type	observed unspiked	observed spiked	spike recovered	spike added	percent recovery
Oligotrophic surface	0.58	5.96	5.34	4.86	110%
	0.54	5.84	5.22	5.49	95%
	---	5.51	4.89	5.00	98%
Deionized water	<0.05	4.59	4.59	4.48	103%
	<0.05	4.28	4.28	4.41	97%
	---	4.66	4.66	4.89	95%
Little Rock, 9m (sulfidic)	11.35	19.68	8.35	9.38	89%
	11.31	22.83	11.50	11.79	98%
	11.33	21.23	9.90	11.03	90%
Polluted, eutrophic	7.70	12.24	4.82	5.10	95%
	7.14	12.43	5.01	4.96	101%
	---	12.33	4.91	4.85	101%
Brown-water Bog	6.01	14.7	8.7	10.0	87%
	5.93	15.7	9.7	10.7	91%
	---	15.8	9.8	10.7	92%

10.0 REFERENCES

Bloom, N.S and Crecelius, E.A. (1983) "Determination of Mercury in Seawater at Subnanogram per Litre Levels". *Mar. Chem.* **14: 49.**

Bloom, N.S and Fitzgerald, W.F. (1988) "Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection". *Anal. Chim. Acta.* **208**: 151.

Fitzgerald, W.F. and Gill, G.A. (1979) "Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis". *Anal. Chem.* 15: 1714.

Gill, G.A. and Fitzgerald, W.F. (1985) "Mercury Sampling of Open Ocean Waters at the Picogram Level". *Deep Sea Res.* 32: 287.

Cossa, D. and Couran, P. (1990) "An International Intercomparison Exercise for Total Mercury in Seawater." *App. Organomet. Chem.* **4**: 49.

MERCURY ANALYSES IN SOLIDS (FRONTIER GEOSCIENCES LOW DETECTION LIMIT METHOD)

Total Mercury In Solids

1.0 SCOPE AND APPLICATION

1.1 This method is a peer-reviewed, published procedure for the determination of total mercury in a wide range of biological and geological matrices. All samples must be subjected to an appropriate dissolution or leaching step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid samples must be prepared according to the procedure discussed in this method.

2.2 This method is a cold vapor atomic fluorescence technique, based upon the emission of 253.7 nm radiation by excited Hg^0 atoms in an inert gas stream. Mercuric ions in the oxidized sample are reduced to Hg^0 with $SnCl_2$, and then purged onto gold-coated sand traps as a means of preconcentration and interference removal. Mercury vapor is thermally desorbed to a second ("analytical") gold trap, and from that into the fluorescence cell. Fluorescence (peak height or area) is measured as a function of total mercury collected, which is converted to concentration by the size of the aliquot purged.

2.3 The typical detection limit for the method is 0.001 $ug \cdot g^{-1}$ as Hg (i.e.; 0.001 ppm).

3.0 INTERFERENCES

3.1 Due to the strong oxidation step, followed by dual gold amalgamation, there are no observed interferences with the method.

3.2 The potential exists for destruction of the gold traps (and consequently low values) if free halogens are purged onto them, or if they are overheated (>500 ^oC). When these instructions are followed accurately, neither of these outcomes is likely.

3.3 Water vapor may collect in the gold traps, and be released into the fluorescence cell where it condenses, giving a false peak due to scattering of the excitation radiation. This can be avoided with the gold trap pre-drying step, and by discarding traps which tend to absorb large quantities of water vapor.

3.4 As always with atomic fluorescence, the fluorescent intensity is strongly dependent upon the inertness of the carrier gas. The dual amalgamation technique eliminates quenching due to trace gases, but it still remains the analyst's responsibility to ensure high purity inert carrier gas and a leak-free analytical train.

4.0 APPARATUS AND MATERIALS

4.1 Atomic fluorescence spectrophotometer or equivalent. To achieve the low detection levels and small, interference-free sample aliquots claimed by this method, a very sensitive CVAFS detector is required. Such systems can be built in-lab according to Bloom and Fitzgerald (1988). Other mercury specific detectors such as atomic absorption or plasma emission may be used, but detection limits would be 10-100 times higher. The CVAFS detector contains the following four major components:

- 4.1.1 Four-watt low pressure mercury vapor lamp.
- 4.1.2 Far UV quartz flow-through fluorescence cell 12 mm x 12 mm x 45 mm long, with a 10 mm path length.
- 4.1.3 UV-visible photomultiplier: sensitive to <230 nm. This PMT is isolated from outside light with a 254 nm interference filter.
- 4.1.4 Flowmeter: flowmeter with needle valve capable of reproducibly keeping carrier gas flow at 30 $mL \cdot min^{-1}$.

4.2 Flow meter/needle valve: capable of controlling and measuring gas flow to the purge vessel at 200-500 $mL \cdot min^{-1}$.

4.3 Teflon fittings: Connections between components and column are made using 6.4 mm O.D. teflon FEP tubing, and teflon friction-fit or threaded

tubing connectors. Connections between components requiring mobility are made with 3.2 mm O.D. teflon tubing due to its greater flexibility.

4.4 Acid fume pretrap: A 10 cm x 0.9 cm diameter teflon tube containing 2-3 grams of reagent grade, non-indicating 8-14 mesh soda lime chunks, packed in between wads of silanized glass wool. This trap is purged of Hg by placing on the output of a clean cold vapor generator, filled with 1% HCl in water , and purging overnight N_2 at 100 $mL \cdot min^{-1}$.

4.5 Cold vapor generator: A 250 mL or 125 mL Florence flask with standard taper 24/40 neck, fitted with a spurging stopper having a coarse glass frit which extends to within 0.2 cm of the flask bottom.

4.6 Gold-coated sand columns: Made from 10 cm lengths of 6.5 mm O.D. x 4 mm I.D. quartz tubing, with a coarse quartz frit 2.0 cm from one end. The tube is filled with 3.4 cm of gold-coated ashed (800 C for 6 hours) quartz sand (60/80 mesh). The end is then plugged with quartz wool. Gold is applied to the sand as a coating several atoms thick using an ion discharge gilding apparatus such as is employed to coat electron microscopy samples. Columns are heated to 450-500 C (a barely visible red glow when the room is darkened) with a coil consisting of 75 cm of 24 ga Nichrome wire at a potential of 10 VAC. Potential is applied and finely adjusted with an auto transformer.

4.7 Recorder: Any multi-range chart recorder or integrator with 0.1-5.000 mV input and variable speeds is acceptable.

4.8 Pipetters: All plastic pneumatic fixed volume and variable pipetters in the range of 10 uL to 5.0 mL.

4.9 Refluxing digestion flask. 100 mL volumetric flasks with acid-cleaned 1-inch diameter glass marbles over the mouth. When the flasks are placed on a hot plate (about 250-350 C) the contents will reflux, the marbles acting as pressure release valves.

5.0 REAGENTS

5.1 Water: 18 megohm ultra pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. As a final mercury and organic removal step, the activated carbon cartridge on the 18 megohm system is placed between the final ion exchange bed and the 0.2 uM filter. Water should be monitored for Hg--especially after ion exchange beds are changed.

5.2 Nitric/sulfuric acid: Carefully add 300 mL of pre-analyzed low mercury (<10 $ng \cdot L^{-1}$ Hg) concentrated sulfuric acid to 750 mL pre-analyzed, low mercury concentrated nitric acid, in a teflon bottle, with constant stirring. *CAUTION: THIS MIXTURE GETS HOT AND EMITS CAUSTIC FUMES.*

5.3 Stannous Chloride: A solution containing 200 g of $SnCl_2 \cdot 2H_2O$ and 100 mL concentrated HCl is brought to 1.0 L with high purity water. This solution is purged overnight with mercury-free N_2 at 500 $mL \cdot min^{-1}$ to remove all traces of Hg. Store tightly capped, and in the dark.

5.4 Bromine monochloride: 45 g of KBr are added to a 2.5 L bottle of concentrated HCl analyzed and found to be low in Hg (<5 $ng \cdot L^{-1}$ Hg). A clean magnetic stir bar is placed in the bottle, and it is stirred for 1 hour in a fume hood. Next, 30 g of pre-analyzed, low Hg $KBrO_3$ are slowly added to the acid with stirring. CAUTION: THIS PROCESS GENERATES COPIUS QUANTITIES OF FREE Cl_2 WHICH ARE RELEASED FROM THE BOTTLE. ADD THE $KBrO_3$ *SLOWLY* AND IN A WELL OPERATING FUME HOOD. When all of the $KBrO_3$ has been added, the solution should have gone from yellow to red to orange. Loosely cap the bottle, and allow to stir another hour before tightening the lid. CAUTION: THE FUMES FROM THIS REAGENT, LIKE CHLORINE OR BROMINE, ARE VERY IRRITATING AND CORROSIVE.

5.5 Stock mercury standard: A commercially available 1000 $mg \cdot L^{-1}$ mercury atomic absorption standard is commonly used. Alternatively, g of high purity $HgCl_2$ may be dissolved in 75 mL of water, 5 mL of bromine monochloride solution added, and the volume brought to 100.0 mL in a class A volumetric flask.

5.6 Mercury secondary standard solution: 0.100 mL of the stock solution is diluted to 100.0 mL of water containing 5 mL of bromine monochloride. The solution contains 1.00 ug·mL^{-1} Hg. Keep in a tightly closed teflon bottle. This solution should be replaced or re standardized yearly.

5.7 Mercury working standard: 1.00 mL of the mercury secondary standard is diluted to 100.0 mL in a class A volumetric flask with high purity water containing 1% by volume bromine monochloride solution. This solution contains 10.0 ng·mL^{-1} and should be replaced monthly.

5.8 Nitrogen: Grade 4.5 (standard laboratory grade) nitrogen which has been further purified by the removal of Hg using a gold-coated sand trap.

5.9 Helium or argon: Grade 5.0 (ultra high purity, G.C. grade) inert gas which has been further purified by the removal of Hg using a gold-coated sand trap.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples should be collected into acid-cleaned teflon or glass bottles with teflon lids. Under no circumstances should polyethylene, polypropylene, or vinyl containers be used.

6.2 Samples are to be frozen at <-10 C (ordinary freezer at lowest setting) until use. A maximum holding time of 1 year at <-10 C is recommended).

6.3 All dissection, homogenization, and other handling of the samples is to occur by clean-room gloved personnel in a class-100 clean station with mercury removal filters.

7.0 PROCEDURE

7.1 Sample preparation. Dissect and homogenize the sample or a greater than 10 g aliquot with acid-washed stainless steel tools. An approximately 1.0 gram aliquot of the homogenized sample is weighed directly into the

volumetric flask. If necessary, up to 2 -3 mL of high purity water may be used to rinse the sample down the bottom. 10.0 mL of the HNO_3/H_2SO_4 mixture are pipetted in, and the sample swirled. The marble is placed over the mouth, and the samples allowed to pre-digest at room temperature for about 1 hour. Samples are next placed on a hot plate, and brought up to a refluxing boil in temperature increments. This is to avoid excessive foaming, especially common with tissue samples. Samples refluxed (hot plate temperature ~300 C) for 2-3 hours, or until all organic matter is dissolved, the solution looks substantially colorless or light yellow, and the brown gas above the liquid has almost disappeared. Sediment samples, especially sandy ones, may take less time. The samples are rinsed in a beaker of water. Samples are diluted to the 100.0 mL mark with high purity water containing 1.0% BrCl. The original volumetric flask caps are replaced, and the samples thoroughly homogenized prior to analysis. Experience and numerous inter calibrations show that undigested rock material or animal fat does not effect the accuracy of this digestion for Hg, because these fractions are very low in initial Hg content, and also are effectively leached by the boiling acid.

7.2 Analysis: 100 mL of water is placed in the bubblers, and 1.0 mL of $SnCl_2$ solution added. The bubbler is purged with N_2 at 350 $mL \cdot min^{-1}$ for 20 minutes, and then a gold-coated sand column is connected to the soda lime pretrap and purged for another 20 minutes. This value is the bubbler blank. To analyze samples, 0.5 mL of $SnCl_2$ and an aliquot of the digestate, usually in the range of 0.25-1.0 mL are pipetted into each bubbler. The caps are replaced, the vessel gently swirled, gold-coated sand columns placed onto the soda lime pretrap outlet, and the sample bubbled for 20 minutes. New samples may then be added to the bubblers, with additional aliquots of $SnCl_2$, up to a maximum of 5 consecutive samples. After 5 samples, the bubbler blanks should be measured, and then the standards. Then the water in the bubblers is replaced with fresh ultra pure water, and the above sequence is repeated.

To analyze the mercury contained on a gold column, the Nichrome wire coil is placed around the column, and the column is inserted in the analyzer train between the incoming Hg-free helium and the second ("analytical") gold-coated sand column. Helium is allowed to pass through the column at a setting of about 30 $mL \cdot min^{-1}$ for 2 minutes to dry off condensed water vapor. Electrical current (10 VAC) is then applied to the coil for 4.0 minutes,

thermally desorbing the Hg as Hg^0, which is carried by the He to the analytical gold column. After 4 minutes, the Nichrome coil is turned off, and a cooling fan directed toward the hot column. Next, the power to the Nichrome wire coil around the analytical column is turned on as is the integrator or other data acquisition device. This column is heated for 3.0 minutes, or 1 minute beyond the point that the peak returns to baseline.

Following the recording of the peak, the analytical trap coil is turned off, and the cooling fan directed at it. The sample trap is now removed from the gas stream, and the teflon end plugs replaced until they are needed to collect another sample. The next sample column is placed in line, and the procedure repeated. Under no circumstances should a sample column be heated while the analytical column is still warm, or analyte may be lost by passing through the analytical column.

Peaks generated using this technique should be very sharp and almost symmetrical. The peak comes off at approximately 1 minute, and has a half-height width of about 5 seconds. Broad or asymmetrical peaks are indicative of an analytical problem, possibly including: low gas flow, water vapor on the column, or an analytical column damaged by chemical fumes or overheating. The last possibility is definitely the case if following a sharp peak, a secondary small broad peak is observed. If the analytical column has been damaged, it and the teflon tubing downstream from it should be discarded, due to the possibility of gold migration on downstream surfaces.

7.3 Cold Vapor Atomic Fluorescence for mercury is linear over at least 5 orders of magnitude (Bloom and Fitzgerald, 1988). However, it is recommended that a 3 point calibration curve, using the method of standard additions, and bracketing the analyte concentrations be prepared each day prior to analyses, to verify linearity.

7.4 This methodology is virtually interference-free, so the method of standard additions is not routinely applied. To run standards, aliquots of working standard solution in the range of 1 ng Hg are injected into a purged bubbler containing a fresh 0.5 mL aliquot of $SnCl_2$, and the analysis run as a sample.

7.5 Gold-coated sand columns should be kept track of by unique identifiers, so that any trap producing poor results can be quickly recognized and discarded. Occasionally due to inadvertent contact with halogen fumes, bubbler solution, organic fumes, or overheating, a sampling column will become damaged; giving low and irreproducible results. Suspect columns should be checked with at least 2 consecutive standard runs before continued use.

7.6 The major cause of analytical problems with this method is from using the soda lime pretraps too long. These traps should be purged overnight as described and then used for only one day's analytical work. Longer use risks irreproducibility, as the traps may begin retarding the flow of Hg^0. Also, as they become very wet, there is a risk of NaOH- saturated water drops coming out onto the gold trap.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed, as discussed in section 8.

7.8 Calculations may be made by reading off of the (linear) standard curve, or by the following method, which is functionally the same:

a) For each net standard result (peak height of standard minus mean peak height of bubbler blanks), divide by the ng of Hg in that spike, to yield the "peak height/ng Hg". Pool all of the "peak height/ng Hg" values for a given sample run when these results are statistically the same, to obtain a mean "peak height/ng Hg" value (A). A is also equal to the slope of the regression of the standard curve.

b) Pool the blank values to obtain a mean "peak height/aliquot of the blank" (B).

c) To calculate the concentration of total mercury in a sample, employ the following formula:

$$\text{Hg (ppm)} = \frac{V(S-B)}{A \cdot v \cdot M \cdot 1000}$$

where V is the final dilution volume of the digestate in mL (in this case, 100 mL), v is the sample aliquot size in mL, S is the gross sample peak height, and M is the digested sample mass, in grams.

d) The detection limit is considered to be 3 times the standard deviation of the method blank.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration data must be composed of a minimum of 3 blanks and 3 standards. Such a calibration should be run at least once per day, or every 20 samples, whichever comes first.

8.3 Samples containing high analyte concentrations may be run either following dilution, or on a separate run at lower instrumental sensitivity.

8.4 A minimum of 3 procedural blanks per batch of 20 samples must be run to obtain a meaningful value for the reporting limits of detection.

8.5 Duplicate or triplicate analyses (depending upon client preference) should be run once every 10 samples or once per batch, whichever comes first.

8.6 NRCC or NBS certified standard materials for mercury in tissues and sediments should be analyzed at a frequency of once per 10 samples or once per batch, whichever comes first.

8.7 Procedural spike recoveries should be run once per 10 samples or once per batch, whichever comes first; in the absence of a suitable certified standard tissue, or at the request of the client.

9.0 METHOD PERFORMANCE

9.1 The data shown in Table 1 indicate the performance of this technique compared to an entirely independent methodology. The data shown in Table 2 further illustrate the precision and accuracy of the method over a wide range of tissue concentrations.

Table 1. Summary of total mercury analysis of NRCC (National Research Council of Canada) certified marine animal tissues

	TORT-1 Hepatopancreas	DORM-1 Dogfish Muscle	DORT-1 Dogfish Liver
(a) Measured			
mean	0.276	0.813	0.230
SD	0.018	0.029	0.011
N	6	6	5
(b) Certified			
mean	0.33	0.798	0.235
SD	0.06	0.074	0.037

Table 2. Mercury levels in several marine and freshwater fish (Bloom, 1989)

Fish Species	Replicates	Mercury concentrations ($ug \cdot g^{-1}$ wet weight) Methylmercury	Total Mercury	Methyl Hg (%)
Chinook Salmon	5	0.0418 ± 0.0042	0.0430 ± 0.0031	97.2
Pacific Halibut	4	0.0555 ± 0.0080	0.0653 ± 0.0018	85.0
Yellow Perch	3	0.526 ± 0.070	0.586 ± 0.026	92.3
White Sucker	3	0.249 ± 0.008	0.231 ± 0.015	107.8
Northern Pike	3	1.762 ± 0.072	1.661 ± 0.043	106.1

10.0 REFERENCES

Bloom, N.S (1983) "Determination of Silver in Marine Sediments by Zeeman-Corrected Graphite Furnace Atomic Absorption Spectroscopy". *Atom. Spectros.* 4: 204.

Bloom, N. (1989) "Determination of Picogram Levels of Methylmercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapor Atomic Fluorescence Detection". *Can. J. Fish Aq. Sci.* 7: 1131.

Bloom, N.S and Crecelius, E.A. (1983) "Determination of Mercury in Seawater at Subnanogram per Litre Levels". *Mar. Chem.* 14: 49.

Bloom, N.S and Crecelius, E.A. (1987) "Distribution of Silver, Mercury, Lead, Copper and Cadmium in Central Puget Sound Sediments". *Mar. Chem.* 21: 377.

Bloom, N.S and Fitzgerald, W.F. (1988) "Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapour Atomic Fluorescence Detection". *Anal. Chim. Acta.* 208: 151.

Fitzgerald, W.F., and Gill, G.A. (1979) "Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis". *Anal. Chem.* 15: 1714.

DDTr AND HCB ANALYSES IN WATER AND SOIL/SEDIMENT (BATTELLE MODIFIED SW-846 LOW DETECTION LIMIT METHOD)

DDTr AND HCB ANALYSES IN WATER AND SOIL/SEDIMENT (BATTELLE MODIFIED SW-846 LOW DETECTION LIMIT METHOD)

The following Modified SW-846 Method will be used by Battelle Marine Science Laboratory in Sequim, Washington for the water and soil/sediment DDTr and HCB analysis. This description was provided by Battelle.

Sediment samples are extracted for pesticide analysis following Battelle SOP MSL-M-079[1] "Extraction and Cleanup of Sediments and Tissues for Semivolatile Organics Following the Surrogate Internal Standard Method" and waters are extracted for pesticides following SOP MSL-M-080[1] "Extraction and Cleanup of waters for Semivolatile Organics Following the Surrogate Internal Standard Method." These methods are based on EPA method 3510 and 8080 (EPA 1986) and NOAA status and trends methodology (Krahn et al. 1988). A 20 gram aliquot of sediment is mixed with sodium sulfate and extracted with methylene chloride in a glass jar on a roller at ambient temperatures. Two PCB congeners (PCB 103 and PCG 198) are added as surrogate internal standards prior to extraction to assess the efficiency of extraction. Sample results are also corrected for the recovery of these compounds. interferences are removed from the extracts using an alumina/silica gel cleanup column. The analytes of interest are eluted with methylene chloride and concentrated column. The analytes of interest are eluted with methylene chloride and concentrated, using Kuderna-Danish (KD) techniques followed by gentle evaporation with nitrogen gas. A portion of this extract is then passed through size-exclusion/gel-permeation high-performance liquid chromatography (HPLC) to remove any remaining interferences. Water samples are extracted with methylene chloride by shaking in a separatory funnel. Sample extracts are then transferred to methyl-t butyl ether (MTBE) and concentrated and analyzed using gas chromatography with electron capture detection (GC-ECD) following SOP MSL-M-044[1] "Analysis of PCBs and chlorinated pesticides by GC/ECD." This is a modified version of EPA SW-846 Method 8080 (EPA 1986). A second, dissimilar

[1]Battelle commonly does not provide their Standard Operating Procedures (SOPs) to be included in work plans. However, these documents can be provided to EPA if requested.

column is used to confirm all pesticide hits on the primary column. The primary column used is a J&W DB-17 and the confirmatory column is a DB-1701, both capillary columns (30 m x 0.25 mm I.D.).

References

Krahn, et al. 1988. "New HPLC Cleanup and Revised Extraction Procedures for Organic contaminants," NOAA Technical Memorandum NMFS F/NWC-153.

U.S. Environmental Protection Agency (EPA). 1986. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846. U.S. Document No. 955-001-00000, U.S. EPA, Washington D.C.

PROTOCOL 3

COPC BIOLOGICAL SAMPLE COLLECTION AND PREPARATION

1.0 PURPOSE

The purpose of the contaminant residual study is to measure the concentrations of ecological chemicals of potential concern (COPCs) in biological samples and to describe the collection methods for biotic samples and their preparation for laboratory analyses. The specific media includes:

- Fish (largemouth bass and mosquitofish)
- Amphibians (bullfrog)
- Mammals (raccoon)
- Birds (little blue heron and warbler, [eggs, and nestlings])
- Invertebrates (crayfish, freshwater mussels and composited terrestrial insect samples)

The main objectives of the sample collection and preparation for this study are to provide comparable data for evaluation of OU-2 and the reference area, exposure assessment data for a quantitative ecological risk assessment, and a database for subsequent monitoring.

2.0 METHODS

Organic contaminants are not evenly distributed throughout biological tissue. Therefore, to obtain homogeneity, all biological samples must be ground (i.e., homogenized) to a similar consistency. Decontamination procedures must follow the processing of each sample and will follow this format:

- Gross wash (soap and water);
- Deionized water rinse;

- Methanol rinse (at least reagent grade methanol); and
- Final deionized water rinse.

2.1 Fish

Largemouth bass will be collected by electrofishing, entangling nets, or hook/line methods. External examination will include condition of eyes, gills, fins, and opercles for deformities. Examination for scars, scale loss, parasites, and skin lesions or tumors will also be conducted. Finally, the removal of the otoliths for determination of age will be performed on the largemouth bass. All observations in the field will be recorded in the field log book. Whole fish will be utilized for COPC analysis, each of which will be a replicate. Multiple specimens will be required for a composite of mosquito fish; the number will be determined in the field and applied uniformly.

The following description has been taken directly or modified from Klemm et al. (1993):

> Chop the fish into cubes unless the sample is small enough to fit in a hand crank meat grinder or a food processor. Pass the whole sample through the grinder. (This process may be facilitated by using partially frozen tissue.) Divide the ground sample into quarters; opposite quarters are mixed by hand with a clean spatula. The two halves are mixed back together. Repeat the mechanical grinding, quartering and hand mixing two more times. Note: No chunks of tissue should be present at this point.

When compositing whole fish, each individual will be ground separately following the above described procedure. Then equal amounts from each fish sample will be composited to provide a total equal to that required for extraction, or the total number of split and archived samples, required by the study plan. Mosquito fish are so small that this step may not be necessary and several whole fish may be composited and processed together.

A minimum 20.0 gram portion of the homogenized tissue will be placed into a sample jar and the jar will be tightly sealed. This process will be repeated with additional containers for duplicates, splits, or archived samples. Each jar will have a unique

sample tag containing the information described in Section 3.2 of the Work Plan. The samples will be transported frozen to Hazleton Environmental Services for analyses with proper chain-of-custody forms included as described in Section 3.4 of the Work Plan.

2.2 Amphibians

Bullfrogs will be collected by hand, dip nets, or gigging at night under hand held lights. If a bullfrog is alive, the frog will be euthanized by pithing prior to a general physical examination. External examination will include observing conditions of eyes, limbs, and mouth for deformities. The skin surface for scars, lesions, tumors, and parasites. The sex and maturation status of each specimen will be determined. All field data will be recorded in the field log book. Whole bullfrogs will be utilized for COPC analysis, each of which will be a replicate.

Sample preparation will follow the procedures listed above for fish sample preparation. Whole body COPC concentrations will be analyzed.

2.3 Mammals

Raccoons will be collected using live traps. Havahart, or equivalent, commercial traps or homemade box traps will be used. These will be baited and set along areas frequented by raccoons. The raccoons will be euthanized by cervical dislocation. Immediately following euthanasia, raccoons will be physically examined. External examination will include noting the condition of fur, eyes, limbs, and movement of joints for deformities. Each specimen will be examined for scars, fur loss, parasites, or tumors. The sex and status of maturation of each specimen will be determined to the extent possible. All field data will be recorded in the field log book. Whole raccoons will be used for COPC analysis. In addition, samples will be collected for analysis of raccoon hair from the same animals used for whole body analysis.

Sample preparation will generally follow the procedures listed above for fish sample preparation. The procedures will be modified to incorporate hair samples for COPC analysis.

2.4 Birds

Little blue herons will be collected by use of nets or guns using "bird shot". If a heron is alive, the bird will euthanized by cervical dislocation and then physically examined. External examination will include noting condition of feathers, eyes, beak, wings and movement of joints for deformities. The skin surface will be examined for scars, feather loss, parasites, or tumors. The sex and state of maturation of each specimen will be determined. All field data will be recorded in the field log book. Whole body samples and feathers will be utilized for COPC analysis. Samples of feathers will be separate or independent of whole body COPC samples but from the same birds.

Sample preparation will generally follow the procedures listed above for fish sample preparation. The procedures will be modified to incorporate feathers for analysis in addition to whole specimens. It may be necessary to composite feathers in order to obtain sufficient weight for analysis.

Prothonotary warbler eggs and fledglings will be collected from managed, artificial, box nesting sites. The nesting boxes for the prothonotary warbler (*Protonotaria citrea*) will be similar to those used by the Fish and Wildlife Service in the OU-2 area. Nesting boxes will also be monitored as to occupancy, clutch size, and hatching success in OU-2 and a reference site if possible. The fledgling sample preparation will follow the procedures listed above for fish sample preparation. Whole body COPC concentrations will be analyzed along with composite egg samples. It may also be necessary to composite fledglings to obtain sufficient sample weight to meet detection limit requirements.

2.5 Invertebrates

The representative, dominant, freshwater mussel species will be collected by hand while wading or using SCUBA gear (see Protocol 4). Insects will be collected primarily with light traps supplemented by sweep nets as required. Crayfish will be collected using baited commercial crayfish traps. Traps will be checked daily and the catch removed. Each catch will be bagged separately. Composite samples may be necessary to obtain

adequate sample weight. Whole "body" invertebrate samples will be analyzed for the COPCs including the carapace of crayfish.

Sample preparation will generally follow the procedures, with slight modifications, listed above for fish sample preparation. Whole body, composite, samples will be used for the crayfish and insect analyses. The mussel shells should be washed thoroughly and rinsed with distilled water. The shell will be opened with a stainless steel knife and all the contents (fluids and tissues) will be placed into the sample jar. The sample will be a composite of five (5) age Class I (1-4 years old) mussels (minimum of 50 grams). Sample sizes should remain constant whenever possible. Shells for each sample should be labeled and retained as discrete samples.

3.0 RESULTS

These analyses will provide additional information regarding the presence of COPCs in the biotic media of OU-2 and the reference area.

4.0 EQUIPMENT

Heavy-duty stainless steel food grinder
Heavy-duty meat cutting bandsaw
Pre-cleaned jars/Bottles
Aluminum pie pans
Heavy-duty aluminum foil
Eckman grab sampler
Spoons
Heavy-duty stainless steel blender
Stainless steel knife
Labels
Disposable, wooded sample stirring tools
Trowels
Gloves

5.0 REFERENCES AND BIBLIOGRAPHY

APHA. 1989. Standard methods for examination of Waste and Wastewater. 17TH Ed. American Public Health Association, Washington, DC.

APHA. 1992. Standard methods for examination of Waste and Wastewater. 18TH Ed. American Public Health Association, Washington, DC.

Cunningham, P.A., J.M. McCarthy and D. Zeitlin 1990. Results of the 1989 Census of State Fish/Shellfish Consumption Advisory Programs. Prepared for S.M. Kroner, Assessment and Water Shed Protection.

Hesse, John L. Michigan Department of Public Health, 1990. Summary and Analysis of Existing Sportfish Consumption Advisory Programs in the Great Lakes Basin. The Great Lakes Fish Consumption Advisory Task Force Co-Chaired by H.A. Anderson and L. Liebenstein, State of Wisconsin. Unpublished.

Klemm, D.J., Q.J. Stober, and J.M. Lazorchak. 1993. Fish field and laboratory methods for evaluating the biological integrity of surface waters. EPA/600/R-92/111. Environmental Monitoring Systems Laboratory Office of Modeling, Monitoring Systems, and Quality Assurance Office of Research and Development, Cincinnati, Ohio.

Puget Sound Estuary Program 1986. Recommended Protocols for Measuring Metals in Puget Sound Water, Sediment and Tissue Samples. Prepared by Tetra Tech, Inc., Bellevue, WA. *In*: Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound. U.S. EPA, Region 10, Seattle, WA (Looseleaf).

Puget Sound Estuary Program 1989 (Revised). Recommended Guidelines for Measuring Organic Compounds in Puget Sound Sediment and Tissue Samples. Prepared by Tetra Tech, Inc., Bellevue, WA. *In*: Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound. U.S. EPA, Region 10, Seattle, WA (Looseleaf).

Stephenson, M.D., M. Martin, S.E. Lange, A.R. Flegal and J.H. Martin 1979. California Mussel Watch 1977-78. Volume II: Trace metals concentrations in the California mussel, *Mytilus californianus*. SWRCB Water Quality Monitoring Report No. 79-22. Sacramento, CA.

U.S. EPA, 1989. Assessing Human Health Risks from Chemically Contaminated Fish and Shellfish: A Guidance Manual. EPA-503/8-89-002. Office of Marine and

Estuarine Protection and Office of Water Regulations and Standards, Washington, DC.

U.S. EPA, 1990a. Bioaccumulation of Selected Pollutants in Fish, A National Study Volume I and II. EPA-506/6-90/001. Office of Water Regulations and Standards (WH-552), Washington, DC.

U.S. EPA, 1990b. Extraction and Analysis of Organics in Biological Tissue, Method OB 8/90, U.S. EPA, Environmental Services Division, Region IV, Analytical Support Branch, Athens, GA.

U.S. EPA, 1990c. Manual for the certification of laboratories analyzing drinking water. Criteria and procedures quality assurance. EPA/570/9-90/008. Prepared by the Laboratory Certification Program Revision Committee. Office of Water (WH-550D), Washington, DC.

U.S. EPA, 1991. Manual for the evaluation of laboratories performing aquatic toxicity tests. EPA/600/4-90/031. Klemm, D.J., L.B. Lobring, and W.H. Horning, II. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH.

Woodward-Clyde Consultants. 1991. Amended Work Plan Remedial Investigation (RI)/Feasibility Study (FS) McIntosh Plant Site. Woodward-Clyde Consultants Baton Rouge, Louisiana.

PROTOCOL 4

FRESHWATER MUSSEL SAMPLING

1.0 PURPOSE

Freshwater mussels can be used as indicators of water quality as determined by presence of contaminants in their tissues. Mussels handle a significant amount of water from which they fulfill physiological and nutritional needs and are thus considered good monitors of water quality.

Freshwater mussels are eaten by a variety of wildlife and some wading birds and, therefore, may be an important component of the OU-2 ecosystem foodchain. There is a slight possibility that at least one endangered mussel {*Potamilus (Proptera) inflatus*} may be resident in OU-2 based on its distribution identified in the recently obtained recovery plan and on the presence of bottom or substrate in which it is often found (USFWS, 1993). Presence or absence of this species will be determined.

Therefore, the primary objective of the mussel population studies are to determine the species present, number of each species, biomass of the population, and relative importance in the foodchain, among other parameters. Since mussels are an indicator of good water quality, it is important to determine the extent to which mussels are reproducing in OU-2 or whether they are being brought in by fish in their parasitic stage. In addition the finding of several species of freshwater mussels in the OU-2 in 1993 appears to be very unique. Telephone calls to both the U.S. Fish and Wildlife Service office in Jackson, Mississippi and Daphne, Alabama and the U.S. Corps of Engineers, in Mobile, Alabama indicates they have no recent knowledge of freshwater mussels in this area of the Tombigbee River. The Corps has taken samples just upstream at Tombigbee river mile 65.1 and downstream of Coffeeville Dam and have found no mussels.

2.0 METHODS

Isom and Gooch (1986) discussed the numerous techniques for sampling freshwater mussels including areal or grab samplers, scuba quadrats, scuba line transects, brails, snorkel, wading, rakes. Only scuba quadrats and scuba line transects are potentially useful for sampling mussels in OU-2. Much of the bottom in OU-2 is reportedly soft mud which would not support the quadrat frame and the overall sparsity and distribution of mussels preclude use of scuba quadrats. Therefore, scuba line transects will be used to take quantitative samples of mussels. Qualitative sampling and observation will be used to locate the areas where mussels are present (the sampling universe) prior to selecting the transect sites or stations.

Scuba Line Transect Method

As noted above, Isom and Gooch (1986) discussed the use of the scuba line transect method for quantitative sampling of freshwater mussels. The method is ideal for use in the shallow OU-2 area where large grab samplers would be difficult to use and scuba quadrats would be inappropriate due to the relatively soft substrate in the basin, and the apparently few mussels per unit area, which would be expected.

Following a boat aided visual observation of the basin, three areas will be selected for quantitative sampling. A weighted 100 meter long rope or a chain, or cable, will be positioned on the bottom within areas expected to contain mussels (i.e. the sampling universe) in a straight line or straight line segments. Two scuba divers will enter the water to take each transect sample with one diver on each side of the rope, (or cable if preferred). They will maintain in contact with the cable and swim along the cable collecting mussels within 1 meter reach. At flagged marked intervals of 6 meters, mussels collected and placed in a bag will be attached to a flagged rope or cable for retrieval and processing. Divers should be aware of and make notes on the substrate type between each interval. Mussel data will then be related to the appropriate transect location, depth, and substrate composition.

3.0 RESULTS

An estimate of the total area of OU-2-containing mussels will be made following sampling in order to estimate the numbers and total weight (biomass) of mussels in the basin.

Data to be collected will include species identification, species and total numbers per unit area, age structure, total weight per unit area (biomass and shell), health condition profiles based on gross pathology (presence of lesions or tumors), and presence or absence of parasites. A representative number of mussels will be marked for potential recapture during monitoring. Marks will be made with an "electric pencil" including species, number, and transect location code (e.g., for Elliptio, /(number), /(transect)). Tentative plans are to contain mussels collected in enclosures for one or two future monitoring events.

These data will provide a baseline for future comparisons and for evaluating the current quality of water for mussel propagation and growth and for comparison with three to five reference areas.

Mussel species will be identified using staff expertise and references for the Tombigbee (Mobile Basin) River drainage system. Where there is the least uncertainty of identifications either relic shells or live specimen shells will be retained for identification using the reference collection at the University of Alabama in Tuscaloosa, Alabama or the USFWS office in Daphne, Alabama.

Weights of specimens will be determined to the nearest gm or 0.5 oz.

Health condition of at least three representative species will be conducted on a minimum of five specimens of each species. All data associated with the specimens will be recorded in table or narrative form. The narrative will be based on the parameters to be screened contained in Table 5-1 of Ohio 1989 (Codes Utilized to Record Anomalies in Mussels; see attached).

CODES UTILIZED TO RECORD ANOMALIES IN MUSSELS[1]

Anomaly Code	Description
D	Deformities of body parts.
E	Eroded shells.
L	Lesions, ulcers
T	Tumors
M	Multiple DELT anomalies (e.g. lesions and tumors, etc.) on the same individual mussels.
AL	Water mites - light infestation: with five or fewer attached mites and/or previous attachment sites.
AH	Water mites - heavy infestation with six or more attached mites and/or previous attachment sites.
CL	Leeches - Light infestation; with one more attached leeches and/or previous attachment sites.
F	Fungus.
S	Emaciated (poor condition, thin, lacking form).
Z	Other, not included above.

[1]Adapted from Table 5-1 contained in Ohio EPA (1989)

Twenty specimens of at least three dominant species will be marked for recapture including 10 from each of two age classes (1-4 years) and (5-8 years) for each species. For example, the age class (1) or (5), the species Q (*Quadrula*) or E (*Elliptio*) and the transect number will be engraved on the shell along with the specimen number. (The example would be 1Q11 to 1Q15 and 5Q11 to 5Q15 etc.)

Age classes will be estimated by counting the annual growth arrests on the shell. (Age Class I individuals are from one to four years old. Age Class II individuals are from five to eight years old and Age Class III, all other ages.)

Mussels will be measured with a commercial caliper or one constructed of hardwood with a 15-cm rule (subdivided to mm) mounted on the side. (This latter caliper supports the mussel enabling the user to maintain proper orientation of the animal so that measurements can be made accurately.) Only length will be measured. The hinge ligament will be used as a reference point and held parallel to the base of the caliper for measuring length.

4.0 EQUIPMENT AND SUPPLIES

Generic equipment for the SCUBA line transect method of sampling mussels follows all of which may not be required for this study and/or some modifications required.

Mask and snorkel
Wet or dry suit
Weight belt with lead weights
Regulator with console (gages)
Backpack (SCUBA)
Medic alert tag
Buoyancy compensator
Dive fins
Dive knife
Dive bag
Dive flag
Transect cable(s), 300 meters
marked at 6 meter intervals
Area dive manual with dive log
Utility box, vehicle and boat

Camera
Motor and boat
Dive ladder
Quadrat sampler
Ponar grab
Brail
Dredge
Needham scraper
Nylon mesh collecting bags
Cloth bags (with draw strings)
Labels (waterproof)
Sample containers, plastic (pint, quart)
SCUBA utility box
First aid kit
Dive lights and flash lights
Fire extinguisher
Dive compass
Bottom timer
Scuba tanks
Topographic maps
Rope (30 meters)

5.0 REFERENCES

Allen, W.R. 1914. The Food and Feeding Habits of Freshwater Mussels. Biol. Bull. 27(3):127-146.

Allen, W.R. 1921. Studies of the Biology of Freshwater Mussels. Biol. Bull. 40(4):210-241.

Anonymous. 1980. Mussel-Bound Monitors. Sci. News. 118(17):270.

Brooks, R.B. and M.G. Rumsby. 1965. Biogeochemistry of Trace Element Uptake by some New Zealand Bivalves. Limnol. and Oceanogr. 10:521-527.

Foster, R.B. 1974. The Potential Use of the Freshwater Mussel as a Monitor of Copper. M.S. Thesis. Eastern Mich. Univ. 43pp.

Foster, R.B. and J.M. Bates. 1978. Use of Freshwater Mussels to Monitor Point source Industrial Discharges. Env. Sci Tech. 12(8): 958-962.

Goldberg, E.D. 1965. Minor Elements in Seawater. Chemical Oceanography. Riley and Skivrow, Eds. Acad. Press. London. Chapter 5:163-194.

Goldberg, E.D. 1978. The Mussel Watch. Env. Conserv. 5:101-125.

Isom, B.G. and Gooch, C. "Rationale and Sampling Designs for Freshwater Mussels Unionidae in Streams, Large Rivers, Impoundments and Lakes" ASTM STP 894, Philadelphia. 1986. pp.46-59.

Leard, R.L., et al. 1980. Use of Selected Freshwater Bivalves for Monitoring Organochlorine Pesticide Residues in Major Mississippi Stream Systems,, 1972-73. Pesticide Monitoring J. 14(2):47-52.

Lord, D.A., W.G. Breck, and R.L. Wheeler. 1975. Trace Elements in Molluscs in the Kingston Basin. In Water Quality Parameters. ASTM STP 573.95-111.

NOAA. 1991, NOAA Technical Memorandum NOS. OMA 59. National Status and Trends Program. Rockville, Maryland. 29 pages, Appendices A, B, C, D, and Microfiche. (Sediments).

Stanczykowska, A. et al. 1976. Bivalves As A Factor Effecting Circulation of Matter in Lake Mikolajskie (Poland). Linmologica (Berlin). 10(2):347-352

Stiff, M.J. 1971. The Chemical States of Copper in Polluted Freshwater and a Scheme of Analysis to Differentiate Them. Water Research. 5:585-599.

USWFS. 1993. Inflated Headsplitter Potamilus Inflatus Recovery Plan. (Prepared by James H. Stewart). Jackson, Mississippi. 15p.

PROTOCOL 5

CHEMICAL LIMNOLOGY OF OU-2

1.0 PURPOSE

This protocol describes the methods for collecting additional chemical limnology data from OU-2 and the reference area. The main objective of the sampling and/or measurements is to provide a basis for interpreting the biological observations.

2.0 METHODS

Routine sampling will be performed at six locations within each study area. In OU-2, four stations from the previous RI grid will be used (Figure 1) as well as a representative location in each of the smaller water-bodies north of the basin. A similar array of stations will be established in the reference area.

For purposes of the additional ecological studies of OU-2, the measurements and analyses discussed in this protocol will be performed at the beginning and at the end of the sampling program, estimated to be mid June and mid August. The water column parameters to be measured and the associated standard methods, are listed in Table 1. A summary of special sample or handling requirements, including preservation and recommended or regulatory maximum storage times, can be found in Table 1060:I of APHA (1992). Table II of 40 CFR 136 also lists these requirements.

In each station, the water quality parameters will be sampled or measured within 2 feet below the surface, with the exception of Secchi disk readings and oxidation/reduction (redox) potential. Redox potential will be measured directly above the sediment/water interface. The samples to be sent off site for analysis will either be collected directly into the sample containers provided by the laboratory or will be collected with a Kemmerer, Van Dorn or bomb-type sampler equipped with a positive messenger-activated closing mechanism.

When and where a station is greater than 2 meters deep, *in situ* instruments will be used to obtain vertical profiles for temperature, dissolved oxygen, pH, and conductivity; measurement intervals will be approximately equivalent to 20 percent of the prevailing depth in a given station.

An Ekman grab sediment sample will be collected at each sample location during the two sampling events for total organic carbon (TOC) and particle size. TOC will be analyzed by method 415.1 (U.S. EPA, 1983).

3.0 REFERENCES

APHA 1992. Standard Methods for the Examination of Water and Wastewater. 18th Edition. American Public Health Association

USEPA, 1983. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (Revised March 1983), Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, OH, 1979.

Title 40, Code of Federal Regulations, §136. EPA Regulations on Test Procedures for Analysis of Pollutants. Table II.

TABLE 1

WATER QUALITY PARAMETERS AND METHODS[1]

Chemical Parameter	U.S. EPA Method or Equivalent[1]	Laboratory or Field Test
Oxidation-Reduction	ASTM D1498-76 (1981)	Field
Dissolved Oxygen (mg/l)	360.1	Field
Temperature (°C)	170.1	Field
pH (Std. units)	150.1	Field
Light Transmission (Secchi)	N/A	Field
Conductivity (μMho/cm)	120.1	Field
Sulfate (mg/l)	375.1, 375.3 or 375.4	Laboratory
Hardness as $CaCO_3$ (mg/l)	Std. Methods 2340.B[2]	Laboratory
Total Alkalinity (mg/l)	310.1	Laboratory
Total Suspended Solids (mg/l)	160.2 or Std. Methods 2540D[2]	Laboratory
Total Organic Carbon (mg/l)	415.1	Laboratory

NOTES:

[1]Unless otherwise indicated, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (Revised March 1983), Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati, OH, 1979.

[2]Standard Methods for the Examination of Water and Wastewater, Seventeenth Edition, American Public Health Association, Washington, D.C., 1989.

PROTOCOL 6

SEDIMENTATION AND CURRENT MEASUREMENTS

1.0 PURPOSE

This protocol describes the methods for evaluating the sedimentation rate and water current velocity of the OU-2 basin area. The Olin basin annually becomes flooded by the Tombigbee River during the winter and spring (approximately 4 to 6 months). During these flood periods the basin water elevation increases up to 20 feet over normal basin elevation. During flood events, sediments within the basin have the potential to be transported from the basin and sediments transported by the Tombigbee flood waters may be deposited within the basin. Data collected from the basin during spring 1993 flood conditions indicated that current speeds are insufficient to result in scouring of basin sediments. The data also showed that current speeds are sufficiently high to suggest that significant deposition of river transported sediment loads does not occur in the basin.

Additional investigations are proposed to collect current speed and directional data at river stages both lower and higher than previously measured during the spring 1993 monitoring period, and to obtain quantitative information regarding potential sedimentation in the basin throughout the year. The main objectives of sedimentation and current measurements study include:

- Determination of current speed and direction in the basin over an extended period of time (1 year) using an InterOceans S4 current meter and

- Quantification of sediment deposition and accretion using sedimentation pins and sediment traps.

2.0 METHODS

2.1 S4 Current Meter Deployment

The S4 meters are self-contained data-logging devices with capabilities for measuring magnitude and direction of horizontal current motion. These meters are capable of measuring current direction (±2°) and speed (0.2 cm/sec resolution). Water currents pass through an electromagnetic field created by the meter producing a voltage that is proportional to water velocity past the meter sensor. The voltage is measured using two pairs of electrodes located symmetrically on the equator of the sensor. This enables measurement of both current speed and direction. Data are stored in solid-state instrument memory for subsequent access using an S4-applications software package.

An S4 meter will be deployed along the eastern portion of the basin. This is judged to be the critical area to monitor potential river flow across the levee or across the northern boundaries of the basin during high river stages. An S4 meter will also be deployed near the basin weir on the southern end of the basin to monitor currents during storm events. The meters will be buoyed from a concrete anchor with nylon rope. The length of the rope will be adjusted such that the length from the base of the blocks to the meter sensor is approximately 1 meter; thus, the sensors will be located about 1 meter above the bottom. A suspension buoy will be attached to the top of meter using about 0.5 to 1 meter of rope. This buoy will remain submerged beneath the water surface and will be used to suspend the meter in the water column. A location buoy will also be attached to the anchor by a separate rope to enable subsequent location, and retrieval of the meter for downloading of data.

2.2 Sedimentation Pins

Sedimentation pins are used to obtain detailed local information on erosion and deposition in wetland environments (Letzsch and Frey, 1980 and Pethick and Reed, 1987 in US Department of Interior Technical Report KBPRT-91/01). Erosion or deposition will be assessed by placing sedimentation pins at eight locations in the basin. The pins will consist of steel rods pushed into the substrate. The pins will be placed in arrays of six pins each at locations along the north, northeast, east, southeast, south,

southwest, west and northwest portions of the basin. Positioning of the pins is limited to relatively shallow areas along the perimeter of the basin. Net erosion or sedimentation will be examined at about bimonthly intervals by measuring the distance from the tops of the pins to the surface of the sediment (outside of any local scour holes).

2.3 Sediment Traps

Sediment traps will be used to collect ambient sediment depositional data within the basin in areas that are too deep for the sediment pins to be effective. The traps will consist of one-quart glass jars placed in concrete blocks. The traps will be placed in arrays of three jars at 12 locations in the basin. The traps will be retrieved at periods coinciding with data collected from the sedimentation pins. During each retrieval event, the sediment accumulated in the jars will be measured to the nearest millimeter. If sufficient in volume, the sediment in each array of three jars will be combined and submitted to the laboratory for chemical analysis of mercury, hexachlorobenzene, and DDTr. The traps will then be reset on the substrate for subsequent recovery during the next retrieval event.

3.0 RESULTS

Erosion and deposition will be assessed using the current speed data based on the sediment transport relationship with sediment particle size (assumed to be fine particles in the silt and clay fraction). Sedimentation and erosion data from the sedimentation pin data, and sedimentation information from the sediment traps will be presented to show sedimentation and erosion zones within the basin.